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NEWS	16	JUN 30	STN AnaVist enhanced with database content from EPFULL
NEWS	17	JUL 28	CA/CAPplus patent coverage enhanced
NEWS	18	JUL 28	EPFULL enhanced with additional legal status information from the epoline Register
NEWS	19	JUL 28	IFICDB, IFIPAT, and IFIUDB reloaded with enhancements
NEWS	20	JUL 28	STN Viewer performance improved
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NEWS	22	AUG 13	CA/CAPplus enhanced with printed Chemical Abstracts page images from 1967-1998
NEWS	23	AUG 15	CAOLD to be discontinued on December 31, 2008
NEWS	24	AUG 15	CAPplus currency for Korean patents enhanced
NEWS	25	AUG 25	CA/CAPplus, CASREACT, and IFI and USPAT databases enhanced for more flexible patent number searching
NEWS	26	AUG 27	CAS definition of basic patents expanded to ensure comprehensive access to substance and sequence information

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FILE COVERS 1907 - 18 Sep 2008 VOL 149 ISS 12
FILE LAST UPDATED: 16 Sep 2008 (20080916/ED)

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=> s (?esterification) (L) ((methyl (a) acetate) or (ethyl (a) acetate) or formate or propionate)
126891 ?ESTERIFICATION
1069165 METHYL

```

    717 METHYLS
1069597 METHYL
      (METHYL OR METHYLS)
    979707 ME
    11297 MES
    986913 ME
      (ME OR MES)
1699369 METHYL
      (METHYL OR ME)
    573680 ACETATE
    30105 ACETATES
    586084 ACETATE
      (ACETATE OR ACETATES)
    505356 ETHYL
    43 ETHYLS
    505382 ETHYL
      (ETHYL OR ETHYLS)
    690323 ET
    8598 ETS
    697316 ET
      (ET OR ETS)
1054585 ETHYL
      (ETHYL OR ET)
    573680 ACETATE
    30105 ACETATES
    586084 ACETATE
      (ACETATE OR ACETATES)
    44864 FORMATE
    3678 FORMATES
    46235 FORMATE
      (FORMATE OR FORMATES)
    50853 PROPIONATE
    2073 PROPIONATES
    51923 PROPIONATE
      (PROPIONATE OR PROPIONATES)
L1      2441 (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACETAT
      E) OR FORMATE OR PROPIONATE)

=> s l1 (L) (fat# or oil#)
    324865 FAT#
    970002 OIL#
L2      177 L1 (L) (FAT# OR OIL#)

=> s l2 and (lipase or enzyme)
    53203 LIPASE
    9156 LIPASES
    54630 LIPASE
      (LIPASE OR LIPASES)
    866752 ENZYME
    495514 ENZYMES
    1095254 ENZYME
      (ENZYME OR ENZYMES)
L3      27 L2 AND (LIPASE OR ENZYME)

=> s l3 and fuel
    446610 FUEL
    177049 FUELS

```

501158 FUEL

(FUEL OR FUELS)

L4 14 L3 AND FUEL

=> d 14 1-7 ibib abs

L4 ANSWER 1 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2008:562374 CAPLUS

TITLE: Lipase-catalyzed biodiesel production with methyl acetate as acyl acceptor

AUTHOR(S): Huang, Ying; Yan, Yunjun

CORPORATE SOURCE: School of Life Science & Technology, Huazhong University of Science and Technology, Wuhan, 430074, Peop. Rep. China

SOURCE: Zeitschrift fuer Naturforschung, C: Journal of Biosciences (2008), 63(3/4), 297-302
CODEN: ZNCBDA; ISSN: 0939-5075

PUBLISHER: Verlag der Zeitschrift fuer Naturforschung

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Biodiesel is an alternative diesel fuel made from renewable biol. resources. During the process of biodiesel production, lipase-catalyzed transesterification is a crucial step. However, current techniques using methanol as acyl acceptor have lower enzymic activity; this limits the application of such techniques in large-scale biodiesel production. Furthermore, the lipid feedstock of currently available techniques is limited. In this paper, the technique of lipase-catalyzed transesterification of five different oils for biodiesel production with Me acetate as acyl acceptor was investigated, and the transesterification reaction conditions were optimized. The operation stability of lipase under the obtained optimal conditions was further examined. The results showed that under optimal transesterification conditions, both plant oils and animal fats led to high yields of Me ester: cotton-seed oil, 98%; rape-seed oil, 95%; soybean oil, 91%; tea-seed oil, 92%; and lard, 95%. Crude and refined cotton-seed oil or lard made no significant difference in yields of Me ester. No loss of enzymic activity was detected for lipase after being repeatedly used for 40 cycles (ca. 800 h), which indicates that the operational stability of lipase was fairly good under these conditions. Our results suggest that cotton-seed oil, rape-seed oil and lard might substitute soybean oil as suitable lipid feedstock for biodiesel production. Our results also show that our technique is fit for various lipid feedstocks both from plants and animals, and presents a very promising way for the large-scale biodiesel production.

REFERENCE COUNT: 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2008:128012 CAPLUS

DOCUMENT NUMBER: 148:264711

TITLE: Environmental friendly method for production of biodiesel

INVENTOR(S): Weng, Tianbo

PATENT ASSIGNEE(S): Shanghai CNPC Enterprise Group Co., Ltd., Peop. Rep. China

SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 5pp.
CODEN: CNXXEV
DOCUMENT TYPE: Patent
LANGUAGE: Chinese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	---	-----	-----	-----
CN 101113354	A	20080130	CN 2006-10029460	20060727
PRIORITY APPLN. INFO.:			CN 2006-10029460	20060727

AB The title method comprises the steps of: mixing short-chain fatty acid ester (Me acetate or Et acetate) as the acyl receptor with animal and vegetable oils at a mol. ratio of (3-15):1, and performing transesterification reaction by lipase catalysis for 4-15 h to obtain biodiesel. The method has the advantages of mild reaction conditions, simple process and easy control, and is environmental friendly.

L4 ANSWER 3 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2007:1342659 CAPLUS

DOCUMENT NUMBER: 149:227633

TITLE: Study on rapeseed oil extraction by methyl acetate coupling with lipase-catalyzed transesterification for bio-diesel production

AUTHOR(S): Li, Lilin; Du, Wei; Liu, Dehua; Xu, Yuanyuan

CORPORATE SOURCE: Department of Chemical Engineering, Tsinghua University, Beijing, 100084, Peop. Rep. China

SOURCE: Shipin Yu Fajiao Gongye (2006), 32(5), 5-8

CODEN: SPYYDO; ISSN: 0253-990X

PUBLISHER: Shipin Yu Fajiao Gongye

DOCUMENT TYPE: Journal

LANGUAGE: Chinese

AB Acetate Me could be used as a novel acyl acceptor in the enzymical route for bio-diesel production, with which lipase expresses good stability. Acetate Me was adopted directly as a solvent to extract the oil from rapeseed powder and then the mixture of crude rapeseed oil and Me acetate was transesterified by lipase for bio-diesel production. Three extraction factors (solvent weight, extraction time, extraction temperature) were studied by orthogonal test. Under the optimized conditions, the extraction rate could reach 51%, just as high as that with n-hexane as the extracting solvent, while the PLs content of the oil extracted by Me acetate was only 0.038%, much lower than that with n-hexane as the extracting solvent (PLs has been demonstrated to have some neg. effect on lipase activity). Extracted oil was transesterified with acetate Me catalyzed by lipase to produce bio-diesel and a bio-diesel yield of 92% could be achieved at 12 h reaction.

L4 ANSWER 4 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2007:1152916 CAPLUS

DOCUMENT NUMBER: 148:36089

TITLE: Enzymatic transesterification of olive oil and its precursors

AUTHOR(S): Coggon, Robert; Vasudevan, Palligarnai T.; Sanchez, Fernando

CORPORATE SOURCE: Department of Chemical Engineering, University of New
Hampshire, Durham, NH, 03824, USA
SOURCE: Biocatalysis and Biotransformation (2007), 25(2-4),
135-143
CODEN: BOBOEQ; ISSN: 1024-2422
PUBLISHER: Informa Healthcare
DOCUMENT TYPE: Journal
LANGUAGE: English

AB The effect of different solvents and three different acyl acceptors on the transesterification of triolein (as a model compound) was investigated. The yield of biodiesel (Me or Et ester) was monitored as a function of time. The yield of the product was also determined in a solvent-free system for two different modes of stirring. The results indicate that the highest yield is obtained in a solvent-free system with mech. stirring. Me acetate is also effective as a solvent and acyl acceptor. Biodiesel was also produced by transesterification of triglycerides (triolein) present in olive oil with methanol and Novozym 435. The effect of the molar ratio of methanol to triolein, mode of methanol addition, enzyme activity and reaction temperature on overall conversion and yield was determined. The final conversion and yield of biodiesel after a reaction time of 24 h were unaffected by changes in these parameters over the range studied. Preliminary findings indicate that the results obtained from small scale reactors and fresh oil can be extended to larger reactors and used oil.

REFERENCE COUNT: 12 THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 5 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2007:514630 CAPLUS
DOCUMENT NUMBER: 149:13249
TITLE: Improving enzymatic transformation of waste edible oil to biodiesel by adding organic base
AUTHOR(S): Chen, Zhi-feng; Zong, Min-hua; Wu, Hong
CORPORATE SOURCE: Lab of Applied Biocatalysis, South China University of Technology, Guangzhou, 510640, Peop. Rep. China
SOURCE: ACS Symposium Series (2007), 959(Ultraclean Transportation Fuels), 51-57
CODEN: ACSMC8; ISSN: 0097-6156
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English

AB The transesterification of waste edible oil and Me acetate to biodiesel catalyzed by the immobilized lipase Novozym 435 was explored. Novozym 435 could catalyze the transesterification of waste oil with high free fatty acid (FFA) content ($\leq 27.8\%$) and Me acetate, and Me ester (ME) yield reached 77.5% after a reaction time of 24 h, which was much lower than that with refined corn oil being the raw material (86.2%). FFA was demonstrated to be the major influential factor on the reaction, ME yield dropped sharply with increasing FFA concentration. Acetic acid, the byproduct formed in the transesterification of FFA with Me acetate, was found to be responsible for the decrease of ME yield. Addition of organic base trihydroxymethyl aminomethane and triethylamine at the concentration of 5% based on oil weight to the reaction system could not only speed up the reaction, but

improve ME yield.

REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 6 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:1165163 CAPLUS

DOCUMENT NUMBER: 146:524717

TITLE: Lipase-mediated conversion of vegetable oils into biodiesel using ethyl acetate as acyl acceptor

AUTHOR(S): Modi, Mukesh Kumar; Reddy, J. R. C.; Rao, B. V. S. K.; Prasad, R. B. N.

CORPORATE SOURCE: Division of Lipid Science and Technology, Indian Institute of Chemical Technology, Hyderabad, 500 007, India

SOURCE: Bioresource Technology (2006), Volume Date 2007, 98(6), 1260-1264

CODEN: BIRTEB; ISSN: 0960-8524

PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Et acetate was explored as an acyl acceptor for immobilized lipase-catalyzed preparation of biodiesel from the crude oils of *Jatropha curcas* (jatropha), *Pongamia pinnata* (karanj), and *Helianthus annuus* (sunflower). The optimum reaction conditions for interesterification of the oils with Et acetate were 10% of Novozym-435 (immobilized *Candida antarctica* lipase B) based on oil weight, Et acetate to oil molar ratio of 11:1 and the reaction period of 12 h at 50°. The maximum yield of Et esters was 91.3%, 90%, and 92.7% with crude jatropha, karanj, and sunflower oils, resp., under the above optimum conditions. Reusability of the lipase over repeated cycles in interesterification and ethanolysis was also investigated under standard reaction conditions. The relative activity of lipase could be well maintained over twelve repeated cycles with Et acetate while it reached to zero by the sixth cycle when ethanol was used as an acyl acceptor.

REFERENCE COUNT: 19 THERE ARE 19 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 7 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:1052001 CAPLUS

DOCUMENT NUMBER: 146:299006

TITLE: Application of silica aerogel encapsulated lipases in the synthesis of biodiesel by transesterification

AUTHOR(S): Orcaire, Olivier; Buisson, Paulette; Pierre, Alain C.

CORPORATE SOURCE: Institut de Recherches sur la Catalyse, CNRS-UPR 5401, Universite Claude Bernard-Lyon I, Villeurbanne, Fr.

SOURCE: Journal of Molecular Catalysis B: Enzymatic (2006), 42(3-4), 106-113

CODEN: JMCEF8; ISSN: 1381-1177

PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Two types of com. lipases prepns., one from *Burkholderia cepacia*, the other one from *Candida antarctica*, were encapsulated in silica aerogels reinforced with silica quartz fiber felt and dried by the CO₂

supercrit. technique. These immobilized biocatalysts were applied in biodiesel synthesis by transesterification of sunflower oil with Me acetate. They were efficient even with mixts. of both substrates without any solvent addition. The aerogel encapsulation technique made it possible to maintain the enzymes in a dispersion state similar to the dispersion prevailing in an aqueous solution, even for further use in organic hydrophobic media. In transesterification in excess isooctane, the two lipases encapsulated in aerogels made from 40% MTMS, have activities relatively close to each other and comparable with com. Novozyme 435. On the other in transesterification with mixture of oil and Me acetate without any solvent, the kinetics were severely limited by substrate diffusion inside the aerogels. This was particularly true with the C. antarctica, so that the corresponding aerogel encapsulated enzyme was much less active than com. Novozyme 435, although it improved after a few tests.

REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> d 14 8-14 ibib abs

L4 ANSWER 8 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:345019 CAPLUS

DOCUMENT NUMBER: 144:491788

TITLE: Method for producing biodiesel by enzyme
-catalyzed transesterification of high-acid-number
waste oils

INVENTOR(S): Zong, Minhua; Chen, Zhifeng; Wu, Hong

PATENT ASSIGNEE(S): South China University of Technology, Peop. Rep. China

SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 8 pp.

CODEN: CNXXEV

DOCUMENT TYPE: Patent

LANGUAGE: Chinese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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CN 1730613	A	20060208	CN 2005-10036639	20050819
CN 1325606	C	20070711		

PRIORITY APPLN. INFO.: CN 2005-10036639 20050819

AB The method includes placing C2-6 short-chain aliphatic esters and high-acid number waste oils at a molar ratio of (8-24):3 into a reactor; mixing uniformly; adding (based on oil weight) 5-30% lipase and 5-15% alkaline substance; and reacting on a vibrating bed at 30-60° for 8-48 h, wherein the alkaline substance is selected from triethylamine, potassium carbonate, etc.

L4 ANSWER 9 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2006:331929 CAPLUS

DOCUMENT NUMBER: 145:422251

TITLE: Transesterification of waste oil with high acid value
to biodiesel catalyzed by immobilized lipase

AUTHOR(S): Chen, Zhifeng; Wu, Hong; Zong, Minhua

CORPORATE SOURCE: College of Biological Sciences and Biotechnology,
South China University of Technology, Guangzhou,

SOURCE: Guangdong, 510640, Peop. Rep. China
Cuihua Xuebao (2006), 27(2), 146-150
CODEN: THHPD3; ISSN: 0253-9837
PUBLISHER: Kexue Chubanshe
DOCUMENT TYPE: Journal
LANGUAGE: Chinese

AB The transesterification of waste oil with high acid value and Me acetate to biodiesel catalyzed by the immobilized lipase Novozym 435 was explored. Novozym 435 can catalyze this reaction, and the Me ester (ME) yield reaches 77.5% after reaction for 24 h, which is much lower than that (86.2%) using refined corn oil as the raw material. The effects of water, free fatty acid, and acetic acid in the reaction system on the reaction were systematically studied. Water has little influence on the reaction when its content is lower than 0.05%, while above this value both the ME yield and the reaction rate decrease with increasing water content. Free fatty acid influences the reaction greatly, and the ME yield drops sharply with increasing free fatty acid concentration. Acetic acid, the byproduct formed in the transesterification of free fatty acid with Me acetate, is responsible for the decrease of ME yield. The addition of organic bases such as trihydroxymethyl aminomethane and triethylamine at a concentration of 10% based on the oil mass to the reaction system can not only speed up the reaction, but improve the ME yield as well, with ME yields being 85.9% and 80.8%, resp., after reaction for 12 h. The operational stability of Novozym 435 is improved markedly by the addition of bases. Adding trihydroxymethyl aminomethane and triethylamine to the reaction system leads to a retention of 97% and 93% of the original activity of Novozym 435, resp., after operation of 10 batches, while the control is only 86%.

L4 ANSWER 10 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:844270 CAPLUS
DOCUMENT NUMBER: 143:308992
TITLE: Improving enzymatic transformation of waste edible oil to biodiesel by adding organic base
AUTHOR(S): Chen, Zhi-feng; Zong, Ming-hua; Wu, Hong
CORPORATE SOURCE: Biotechnology Department, South China University of Technology, Guangzhou, 510640, Peop. Rep. China
SOURCE: Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry (2005), 50(2), 809-810
CODEN: PSADFZ; ISSN: 1521-4648
PUBLISHER: American Chemical Society, Division of Fuel Chemistry
DOCUMENT TYPE: Journal; (computer optical disk)
LANGUAGE: English

AB The transesterification of waste edible oil and reformed corn oil was performed with Me acetate and lipase B from Candida Antarctica (Novozym 435), in order to produce biodiesel. The reaction rate and the fatty acid Me ester yield were improved by the addition of organic bases such as tri-hydroxymethyl aminomethane, triethylamine or pyridine.
REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 11 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:391617 CAPLUS
DOCUMENT NUMBER: 142:449357
TITLE: Method for preparing biodiesel from animal or plant

oil
 INVENTOR(S): Du, Wei; Xu, Yuanyuan; Liu, Dehua
 PATENT ASSIGNEE(S): Tsinghua University, Peop. Rep. China
 SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 10 pp.
 CODEN: CNXXEV
 DOCUMENT TYPE: Patent
 LANGUAGE: Chinese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CN 1436834	A	20030820	CN 2003-119600	20030313
WO 2004081158	A1	20040923	WO 2004-CN51	20040115
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
US 20060257986	A1	20061116	US 2006-549336	20060620
PRIORITY APPLN. INFO.:				
			CN 2003-119600	A 20030313
			WO 2004-CN51	W 20040115

AB Biodiesel was prepared by transesterification of animal or plant oil (castor oil, rapeseed oil, soybean oil, or fish oil) with short chain ester (such as Me acetate and Et acetate) at a molar ratio of 1:3-20 in the presence of lipase Novozyme 435 (30% of oil) at 20-60° for 4-20 h.

L4 ANSWER 12 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2005:174218 CAPLUS

DOCUMENT NUMBER: 142:462336

TITLE: Study on the kinetics of enzymatic interesterification of triglycerides for biodiesel production with methyl acetate as the acyl acceptor

AUTHOR(S): Xu, Yuanyuan; Du, Wei; Liu, Dehua

CORPORATE SOURCE: Department of Chemical Engineering, Tsinghua University, Beijing, 100084, Peop. Rep. China

SOURCE: Journal of Molecular Catalysis B: Enzymatic (2005), 32(5-6), 241-245

CODEN: JMCEF8; ISSN: 1381-1177

PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

AB A new route for biodiesel production using Me acetate instead of methanol as the acyl acceptor was proposed in our previous research, and it has been found that this novel route could enhance the stability of the immobilized lipase greatly. In this paper, the kinetics of lipase-catalyzed interesterification of triglycerides for biodiesel production with Me acetate as the acyl acceptor was further studied. First, a simplified model based on Ping Pong Bi Bi with substrate competitive inhibition mechanism was proposed to describe the reaction kinetics of the

interesterification. During our further study, it was observed that three consecutive and reversible reactions occurred in the interesterification of triglycerides and Me acetate. So, a kinetic model based on mass balance of three second-order reversible reactions was developed and the reaction rate constant, k , was determined by solving the differential rate equations of the reaction system. The results showed that k_{DG-MG} (0.1124) and k_{MG-TA} (0.1129) were much higher than k_{TG-DG} (0.0311), which indicated that the first step reaction was the limit step for the overall interesterification.

REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 13 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2004:558567 CAPLUS
DOCUMENT NUMBER: 141:313005
TITLE: Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors
AUTHOR(S): Du, Wei; Xu, Yuanyuan; Liu, Dehua; Zeng, Jing
CORPORATE SOURCE: Department of Chemical Engineering, Tsinghua University, Beijing, 100084, Peop. Rep. China
SOURCE: Journal of Molecular Catalysis B: Enzymatic (2004), 30(3-4), 125-129
CODEN: JMCEF8; ISSN: 1381-1177
PUBLISHER: Elsevier Science B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Me acetate, a novel acyl acceptor for biodiesel production has been developed, and a comparative study on Novozym 435-catalyzed transesterification of soybean oil for biodiesel production with different acyl acceptors was conducted and reported in this paper. Methanol has a serious neg. effect on enzymic activity. A molar ratio of methanol to oil of above 1:1 leads to serious inactivation of the enzyme. However, when Me acetate was used as the acyl acceptor, a yield of 92% of Me ester could be obtained with a molar ratio of Me acetate to oil of 12:1, and Me acetate showed no neg. effect on enzymic activity. Addnl., with crude soybean oil as the oil source and methanol as acyl acceptor, a much lower Me ester yield was obtained than that with refined soybean oil, while with Me acetate as acyl acceptor, an equally high yield of Me ester (92%) was achieved for both soybean oils. Lipase loses its activity very rapidly during repeated expts. with methanol as the acyl acceptor, while there is almost no detected loss in lipase activity, even after being continuously used for 100 batches, when Me acetate was used for biodiesel production. Moreover, the byproduct triacetin is an important chemical with a higher value than glycerol, and this novel acyl acceptor seems very promising for lipase-catalyzed large-scale production of biodiesel.

REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 14 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2003:603489 CAPLUS
DOCUMENT NUMBER: 139:383869
TITLE: A novel enzymatic route for biodiesel production from renewable oils in a solvent-free medium

AUTHOR(S): Xu, Yuanyuan; Du, Wei; Liu, Dehua; Zeng, Jing
CORPORATE SOURCE: Department of Chemical Engineering, Tsinghua
University, Beijing, 100084, Peop. Rep. China
SOURCE: Biotechnology Letters (2003), 25(15), 1239-1241
CODEN: BILED3; ISSN: 0141-5492
PUBLISHER: Kluwer Academic Publishers
DOCUMENT TYPE: Journal
LANGUAGE: English
AB A new enzymic route for biodiesel production from soybean oil was
developed using Me acetate as a novel acyl acceptor.
Novozym 435 (immobilized Candida antarctica lipase) gave the
highest Me ester (ME) yield of 92%. The optimum conditions of the
transesterification were 30% enzyme based on oil
weight; a molar ratio of Me acetate/oil of
12:1; temperature 40° and reaction time 10 h. Since no glycerol was
produced in the process, this method is very convenient for recycling the
catalyst and byproduct triacetyl glycerol showed no neg. effect on the
fuel property.
REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> d his

(FILE 'HOME' ENTERED AT 09:59:01 ON 18 SEP 2008)

FILE 'CAPLUS' ENTERED AT 09:59:39 ON 18 SEP 2008

L1 2441 S (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACE
L2 177 S L1 (L) (FAT# OR OIL#)
L3 27 S L2 AND (LIPASE OR ENZYME)
L4 14 S L3 AND FUEL

=> s l1 (L) (fatty (a) acid (a) alkyl (a) ester)

409031 FATTY

14 FATTIES

409035 FATTY

(FATTY OR FATTIES)

4673506 ACID

1651424 ACIDS

5190793 ACID

(ACID OR ACIDS)

617705 ALKYL

6723 ALKYLs

620746 ALKYL

(ALKYL OR ALKYLs)

628504 ESTER

461618 ESTERS

872282 ESTER

(ESTER OR ESTERS)

L5 3 L1 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)

=> d l5 1-3 ibib abs

L5 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2008:464894 CAPLUS

TITLE: Biodiesel production by supercritical process with
crude bio-methanol prepared by wood gasification

AUTHOR(S): Isayama, Yohei; Saka, Shiro
 CORPORATE SOURCE: Department of Socio-Environmental Energy Science,
 Graduate School of Energy Science, Kyoto University,
 Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan
 SOURCE: Bioresource Technology (2008), 99(11), 4775-4779
 CODEN: BIRTEB; ISSN: 0960-8524
 PUBLISHER: Elsevier Ltd.
 DOCUMENT TYPE: Journal
 LANGUAGE: English

AB In order to prepare a genuine biodiesel, it is essential to use methanol prepared from biomass but not natural gas for biodiesel production. Thus, we have proposed to use crude bio-methanol produced by wood gasification for biodiesel production. Since such a bio-methanol contains some impurities, an effect of its impurities was studied on the biodiesel production by supercrit. method. In general, impurities in crude bio-methanol are reported to include Me formate, ethanol, 1-butanol, diisopropyl ether, water, etc. Triglycerides and oleic acids were, thus, treated with these impurities under supercrit. conditions. As a result, it was found that Me formate, ethanol and 1-butanol could convert them to fatty acid alkyl esters (BDF), whereas no conversion was achieved with diisopropyl ether. Thus, crude bio-methanol can be used for BDF production as a substitute for methanol from fossil resources. However, due to more efficient reaction, crude bio-methanol can be more applicable to the two-step supercrit. methanol process, consisting of hydrolysis of triglycerides and subsequent esterification of fatty acids, compared with the one-step supercrit. methanol process, where transesterification of triglycerides is a major reaction.

REFERENCE COUNT: 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2007:435952 CAPLUS
 DOCUMENT NUMBER: 146:421640
 TITLE: Method for production of fatty acid alkyl ester as
 biodiesel fuel
 INVENTOR(S): Saka, Shiro
 PATENT ASSIGNEE(S): Kyoto University, Japan
 SOURCE: PCT Int. Appl., 59pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2007043567	A1	20070419	WO 2006-JP320295	20061011
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW			
RW:	AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH,			

GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY,
KG, KZ, MD, RU, TJ, TM

JP 2007106689 A 20070426 JP 2005-298162 20051012
JP 2007131595 A 20070531 JP 2005-327942 20051111
JP 2007169173 A 20070705 JP 2005-365631 20051219

PRIORITY APPLN. INFO.:

JP 2005-298162 A 20051012
JP 2005-327942 A 20051111
JP 2005-365631 A 20051219

OTHER SOURCE(S): CASREACT 146:421640; MARPAT 146:421640

AB A process to improve the efficiency of the production of a fatty acid alkyl ester, which is useful as biodiesel fuel, is described. A fatty acid alkyl ester can be produced by performing esterification between a fatty acid and a carboxylic acid ester under predetd. temperature/pressure conditions (step X). The fatty acid may be produced from

a raw oil-and-fat material or a free fatty acid contained in the raw oil-and-fat material through a given process. The given process to be performed prior to the step X may comprises a step of performing transesterification between a fatty acid glyceride contained in the raw oil-and-fat material and a carboxylic acid under predetd. temperature/pressure conditions to yield the desired fatty acid (step A) or a step of hydrolyzing a fatty acid glyceride contained in the raw oil-and-fat material under predetd. temperature/pressure conditions to yield

the desired fatty acid (step B). Thus, a 1:15 mixture of Me formate and oleic acid was heated at 350° for 9 min in a batch reactor under critical conditions to give 93.4% Me oleate. Various esterification conditions were examined using rapeseed oil, methanol (transesterification to give fatty acid esters), Me formate or Et formate, and acetic acid (transesterification to give fatty acids) as well as solubility of reaction mixts. in organic solvent.

REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2000:464963 CAPLUS

DOCUMENT NUMBER: 133:89231

TITLE: Method for preparation of α -sulfo fatty acid alkyl ester salts

INVENTOR(S): Tano, Tetsuo; Yamauchi, Azusa; Nishio, Hiroshi; Matoba, Seiji; Yoshiya, Masahisa

PATENT ASSIGNEE(S): Lion Corp., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 7 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2000191626	A	20000711	JP 1998-371658	19981225
PRIORITY APPLN. INFO.:			JP 1998-371658	19981225

OTHER SOURCE(S): CASREACT 133:89231; MARPAT 133:89231

AB A process for preparation of RCH₂CH(SO₃H)CO₂R₁ salts (R = C₆-24 linear or

branched alkyl or alkenyl; R1 = C1-6 linear or branched alkyl) involves sulfonation of fatty acid alkyl esters represented by formula $\text{RCH}_2\text{CH}_2\text{CO}_2\text{R}_1$ (R, R1 = same as above) and esterification of the resulting crude sulfonic acids with lower alcs., wherein the latter esterification step is carried out by adding lower alcs. and C2-6 fatty ether. This process esterified fatty acid ester-SO₃ (1:2) adducts (impurities), i.e. $\text{RCH}_2\text{CH}(\text{SO}_3\text{H})\text{CO}_2\text{-SO}_2\text{-OR}_1$ using lower alcs. to $\text{RCH}_2\text{CH}(\text{SO}_3\text{H})\text{CO}_2\text{R}_1$ and provides α -sulfo fatty acid alkyl ester salts of improved purity which are light-colored and reduced in odor and are useful as surfactants. Thus, 7 volume% anhydrous SO₃(g) in N was introduced into a 2:8 weight mixture of Me myristate and Me palmitate (iodine value of 0.40) in a 1/1.2 molar ratio of fatty acid ester/SO₃ at 80° over 60 min and the resulting mixture was stirred at 80° for 30 min to give crude α -sulfo fatty ester Me ester containing diadduct impurities (98.0% reaction ratio for the fatty acid Me esters). A MeOH solution containing di-Me ether 10, Me acetate 1, and H₂O 0.1 weight% and H₂O₂ were added to the crude α -sulfo fatty Me ester in 20 and 2.5 weight part of the MeOH solution per 100 part α -sulfo fatty acid Me ester, followed by adding 2.5 weight part H₂O₂. The resulting mixture was stirred at 80° for 155 min for esterification and bleaching and neutralized by aqueous NaOH to pH 7-8 followed by stripping residual alc. on a evaporation dish to give a 67.5 weight% solution of α -sulfo fatty acid Me ester sodium salt,. The latter solution showed slight odor and remained the same after one month, and odor can be masked by perfume.

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(FILE 'HOME' ENTERED AT 09:59:01 ON 18 SEP 2008)

FILE 'CAPLUS' ENTERED AT 09:59:39 ON 18 SEP 2008

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L1      2441 S (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACE
L2      177 S L1 (L) (FAT# OR OIL#)
L3      27 S L2 AND (LIPASE OR ENZYME)
L4      14 S L3 AND FUEL
L5      3 S L1 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)
```

=> s alcoholysis (L) ((methyl (a) acetate) or (ethyl (a) acetate) or formate or propionate)

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7694 ALCOHOLYSIS
1069165 METHYL
717 METHYLS
1069597 METHYL
(METHYL OR METHYLS)
979707 ME
11297 MES
986913 ME
(ME OR MES)
1699369 METHYL
(METHYL OR ME)
573680 ACETATE
30105 ACETATES
586084 ACETATE
(ACETATE OR ACETATES)
505356 ETHYL
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    43 ETHYLS
505382 ETHYL
      (ETHYL OR ETHYLS)
690323 ET
    8598 ETS
697316 ET
      (ET OR ETS)
1054585 ETHYL
      (ETHYL OR ET)
573680 ACETATE
    30105 ACETATES
586084 ACETATE
      (ACETATE OR ACETATES)
44864 FORMATE
    3678 FORMATES
46235 FORMATE
      (FORMATE OR FORMATES)
50853 PROPIONATE
    2073 PROPIONATES
51923 PROPIONATE
      (PROPIONATE OR PROPIONATES)
L6      116 ALCOHOLYSIS (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACETATE) OR
      FORMATE OR PROPIONATE)

=> s 16 (L) (fat# or oil#)
    324865 FAT#
    970002 OIL#
L7      14 L6 (L) (FAT# OR OIL#)

=> s 17 (L) (fatty (a) acid (a) alkyl (a) ester)
    409031 FATTY
    14 FATTIES
    409035 FATTY
      (FATTY OR FATTIES)
4673506 ACID
1651424 ACIDS
5190793 ACID
      (ACID OR ACIDS)
617705 ALKYL
    6723 ALKYLS
620746 ALKYL
      (ALKYL OR ALKYLS)
628504 ESTER
461618 ESTERS
872282 ESTER
      (ESTER OR ESTERS)
L8      0 L7 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)

=> s 17 and fuel
    446610 FUEL
    177049 FUELS
    501158 FUEL
      (FUEL OR FUELS)
L9      0 L7 AND FUEL

=> s 17 and (fatty (a) acid (a) methyl (a) ester)
    409031 FATTY

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      14 FATTIES
409035 FATTY
      (FATTY OR FATTIES)
4673506 ACID
1651424 ACIDS
5190793 ACID
      (ACID OR ACIDS)
1069165 METHYL
      717 METHYLS
1069597 METHYL
      (METHYL OR METHYLS)
      979707 ME
      11297 MES
      986913 ME
      (ME OR MES)
1699369 METHYL
      (METHYL OR ME)
      628504 ESTER
      461618 ESTERS
      872282 ESTER
      (ESTER OR ESTERS)
      5186 FATTY (A) ACID (A) METHYL (A) ESTER
L10      0 L7 AND (FATTY (A) ACID (A) METHYL (A) ESTER)

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=> d his

(FILE 'HOME' ENTERED AT 09:59:01 ON 18 SEP 2008)

FILE 'CAPLUS' ENTERED AT 09:59:39 ON 18 SEP 2008

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L1      2441 S (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACE
L2      177 S L1 (L) (FAT# OR OIL#)
L3      27 S L2 AND (LIPASE OR ENZYME)
L4      14 S L3 AND FUEL
L5      3 S L1 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)
L6      116 S ALCOHOLYSIS (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACETATE)
L7      14 S L6 (L) (FAT# OR OIL#)
L8      0 S L7 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)
L9      0 S L7 AND FUEL
L10     0 S L7 AND (FATTY (A) ACID (A) METHYL (A) ESTER)

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=> d 17 1-7 ibib abs

L7 ANSWER 1 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1981:588695 CAPLUS

DOCUMENT NUMBER: 95:188695

ORIGINAL REFERENCE NO.: 95:31499a,31502a

TITLE: Effect of quality of pentaerythritol on alkyd resin
and its paint

AUTHOR(S): Liu, Zhuangli

CORPORATE SOURCE: Chengchow Paint Co., Chengchow, Peop. Rep. China

SOURCE: Tuliao Gongye (1981), 61, 4-7
CODEN: TLKYD5; ISSN: 0253-4312

DOCUMENT TYPE: Journal

LANGUAGE: Chinese

AB The color of pentaerythritol (I), the content of impurities, and the
content of dipentaerythritol (II) [126-58-9] or polypentaerythritol
affected the synthesis, color, and transparency of alkyd resins. I having

a dark color gave a dark color alkyd resin. II was controlled at .apprx.10%, increasing content of II rapidly increased the viscosity during esterification. Sodium formate [141-53-7] accelerated the alcoholysis of I and vegetable oils, but darkened the resin color and increased turbidity.

L7 ANSWER 2 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1965:411080 CAPLUS
DOCUMENT NUMBER: 63:11080
ORIGINAL REFERENCE NO.: 63:1994c-e
TITLE: Examination of "mono" and technical pentaerythritols and the effect of its impurities on the formulation and properties of alkyds
AUTHOR(S): Thirkel, E.R.
SOURCE: Chim. Peintures (1964), 27(12), 363-8
DOCUMENT TYPE: Journal
LANGUAGE: French

AB The analysis of .apprx.20 com. samples of pentaerythritol (I) is reported; samples containing >97% I and <0.06% ash are classified as "monopentaerythritol" (II), while those containing <96% I, 0.1-0.5% ash, and 3.5-12.4% dipentaerythritol (III) are classified as tech. I. The effect of impurities on color, clarity, alcoholysis and esterification in the manufacture of alkyds with an oil/resin ratio of 65-70% is discussed. A Ca formate content of 0.002-0.004% in I is considered as an allowable limit for maximum gloss and clarity. Linseed oils containing >0.001% Ca gave rise to turbidity in alkyds (measured by comparison with an infusorial earth suspension in H₂O, suitably colored with a solution of I); <0.2% Na formate (calculated as Na₂O) gives no turbidity but frothing during the monoglyceride formation. CaSO₄, Na₂SO₄ and traces of SiO₂ are not harmful. Fe in I rarely exceeds 0.01%; >0.2% Fe formate darkens the color. Traces of inorg. acids leads to the appearance of insol. particles in the resin. The alcoholysis of linseed oil-I-phthalic anhydride alkyds at 265° is catalyzed to a greater extent by Na formate than by Ca formate. Esterification is accelerated by Na formate in tech. I, in contrast to the general opinion attributing such an effect to the high % of III in tech. I. At 230-80° II forms the monoglyceride without the appearance of gelified particles. A conductometric method for the determination of the final point of alcoholysis is more practical than the conventional MeOH tolerance method. By replacing tech. I by II it is possible to reduce the excess of I by 2% and the oil/resin ratio by 0.5%. Alkyds with an oil/resin ratio of 69% can be prepared by saving 8% of II and with no excessive increase in the acid number; drying, pigment-wetting, and film properties are satisfactory. The use of II of low Ca formate content is recommended for alkyds of better color and reproducibility.

L7 ANSWER 3 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1963:59612 CAPLUS
DOCUMENT NUMBER: 58:59612
ORIGINAL REFERENCE NO.: 58:10147e-h,10148a-c
TITLE: 5-Substituted β -(2-furyl)propionic acid esters. Synthesis from β -furfurylidene ketones and their hydrogenation
AUTHOR(S): Thewalt, Klaus; Rudolph, Walter
CORPORATE SOURCE: Chem. Werke Witten, Witten/Ruhr, Germany
SOURCE: Chemische Berichte (1963), 96, 136-42

CODEN: CHBEAM; ISSN: 0009-2940

DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

OTHER SOURCE(S): CASREACT 58:59612

AB The alcoholysis of furfurylideneacetophenone (I) gives good yields of the esters of 3-(5-phenyl-2-furyl)propionic acid (II). This reaction was applied to a series of analogs of I. The hydrogenation of the resulting esters over Raney Ni yields γ -substituted γ -butyrolactones, and over Cu chromite catalyst, ω -substituted alkanediols. Several tech. interesting reactions of the lactones and the diols are described. I (230 g.) in 750 g. BuOH containing 1.5% HCl stirred 24 h. at 100° under N and distilled gave 130 g. yellow, crude ester which was purified by hydrogenation at 100°/20-5 atmospheric over Raney Ni to yield pure Bu ester (III) of II, b₂ 175-80°, m. 14°, n_{20D} 1.5552. III (5.00 g.) saponified with aqueous alc. KOH gave 4.00 g. II, needles, m. 117° (H₂O). III (20 g.) and 5% H₂SO₄ refluxed 2 h. and filtered gave 11 g. BzCH₂CH₂COCH₂CH₂CO₂H, m. 113-14° (H₂O). Furfurylideneacetone (1.5 g.) treated in the usual manner with BuOH, and the resulting pale yellow Bu ester (IV) of 3-(5-methyl-2-furyl)propionic acid (V) saponified with KOH gave 0.80 g. V, needles, m. 56° (H₂O). 1-Benzylidene-3-furfurylideneacetone (60 g.) in 240 cc. absolute BuOH and 50 cc. dry CHCl₃ added during 3 h. dropwise with stirring at 100° to 330 cc. absolute BuOH containing 1.8% HCl and evaporated after an addnl. 3-4 h., and the black, oily residue distilled yielded 18 g. Bu 3-(5-styryl-2-furyl)propionate (VI), b_{0.8} 191-2°. III (300 g.) in MeOH hydrogenated at 150°/85 atmospheric over Raney Ni gave 55 % forerun, b₁ 150-4.5°, and 120 g. tetrahydrofuryl analog (VII) of VI, b₁ 155-55.5°, n_{20D} 1.5008; the forerun containing up to 20% γ -phenylpropyl- γ -butyrolactone (VIII) saponified, acidified, boiled with Ba(OH)2.8H₂O, filtered, and worked up yielded an addnl. 110 g. VII. VII (25 g.) and 2N KOH refluxed 2 h., acidified, and extracted with Et₂O gave 13 g. 3-(5-phenyl-2-tetrahydrofuryl)propionic acid (IX), b₁ 183-5°, n_{20D} 1.5270, m. 32-3° (after 3 mo); S-(p-bromobenzyl)isothiuronium salt m. 126-7°. IX (3 g.) refluxed with 0.9 equivalent Ba(OH)₂ in H₂O and evaporated, and the residue extracted with Et₂O yielded 2.5 g. Ba salt of IX. III (20 g.) in MeOH hydrogenated over Pd-C yielded 14.5 g. VIII, b_{0.6} 152-4°, n_{20D} 1.4772. VIII (5.0 g.) and 3.5 g. Ba(OH)2.8H₂O refluxed 3 h. in H₂O, evaporated, and worked up gave 6.5 g. Ph(CH₂)₃CH(OH)CH₂CH₂CO₂H. IV (10 g.) in MeOH hydrogenated over 1 g. Pd-C yielded 6.5 g. γ -butyl- γ -butyrolactone, b₄ 106-7°, n_{20D} 1.4476. III (200 g.) in dioxane hydrogenated at 200°/250 atmospheric over 20 g. Cu chromite catalyst gave a small forerun of 2-(3-phenylpropyl)tetrahydrofuran (X), and 130 g. Ph(CH₂)₃CH(OH)(CH₂)₃OH (XI), b₁ 169-70°, needles, m. 42°, n_{20D} 1.5126, d₂₆ 1.014; bis(phenylurethane), glass; diacetate b_{0.6} 146-8°, n_{20D} 1.4658. XI (25 g.) and 5 g. dry Al₂O₃ stirred 3 h. at 170° and extracted with Et₂O yielded 14 g. X, b₁ 105-7°, n_{20D} 1.5142. XI (250 g.) and 1000 g. polyphosphoric acid stirred 1 h. at 100-10°, poured into an equal volume H₂O, and extracted with Et₂O gave 160 g. 3-(1,2,3,4-tetrahydro-1-naphthyl)propanol, b₂ 143-4°, n_{20D} 1.5480, d₂₀ 1.047; phenylurethane m. 232-4°; 3,5-dinitrobenzoate, yellowish-tinted, m. 81-2°; Ph₃C ether, yellowish-tinted glass. III (5.0 g.) in 50 cc. dry Et₂O added dropwise with stirring to 1.5 g. LiAlH₄ in 150 cc. dry Et₂O and worked up after 20 min. gave 2.8 g. 3-(5-phenyl-2-furyl)propanol,

yellowish viscous oil, b0.8 142-4°, n20D 1.5859; phenylurethane, slightly yellowish-tinted, m. 80° (petr. ether). VIII (150 g.) in dioxane hydrogenated at 250°/250 atmospheric over Cu chromite gave 60 g. 7-cyclohexylcycloheptanol (XII), b0.8 119-20° [phenylurethane, needles, m. 221-3° (decomposition); 3,5-dinitrobenzoate m. 78°], and 57 g. XI, b0.8 155-7°, n20D 1.4700, d20 0.900. XII (10 g.) added dropwise to 12 g. CrO3 in AcOH, refluxed 2 h., and extracted with Et2O yielded 7.0 g. 7-cyclohexylheptanoic acid, b3 164-8°, m. 26°. XI (200 g.) in dioxane hydrogenated at 190°/200 atmospheric over Raney Ni gave 85% 7-cyclohexylheptane-1,4-diol, b1 160-2°, m. 33°, n30D 1.4798.

L7 ANSWER 4 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1961:13559 CAPLUS

DOCUMENT NUMBER: 55:13559

ORIGINAL REFERENCE NO.: 55:2711b-i,2712a-h

TITLE: An alkaloid of *Dioscorea hispida*, Dennstedt. VI. Some investigations on the synthesis of 2-tropanone

AUTHOR(S): Davies, W. A. M.; Jones, J. B.; Pinder, A. R.

CORPORATE SOURCE: Univ. Coll., Cardiff, UK

SOURCE: Journal of the Chemical Society (1960) 3504-12

CODEN: JCSOA9; ISSN: 0368-1769

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

AB cf. CA 53, 18076c. Possible routes for the synthesis of (±)-2-tropanone (I) were explored. 2-Isobutyl-N,N-dimethylcycloheptylamine (II) was synthesized, probably as a mixture of cis- and trans-forms. II was not identical with the fully hydrogenated Hofmann base from dioscorine. Dioscorinol (III) separated as rhombic prisms, m. 119-20° (C6H6). Ozonolysis of III gave 2β-acetonyl-2α-tropanol (IV), isolated as the picrate, prisms, m. 120° (MeOH). IV (1 g.) kept 24 hrs. with 65 cc. 0.1N NaOH, cooled, saturated with K2CO3, continuously extracted 16 hrs. with Et2O, and distilled gave 0.55 g. I, b14 98°, b17 105-6°, [α]24D 15.0° (c 1.43, H2O); picrate used to give pure I, b14.5 100°. I (0.3 g.) in 15 cc. 2N HCl added to 50 mg. PtO2 prerduced in 10 cc. 2N HCl, the mixture treated with 2 cc. concentrated HCl, the mixture shaken 18 hrs. with H, extracted with Et2O,

and distilled gave 0.25 g. tropane, b92 96°; picrate m. 284-5° (decomposition). Et α-bromocrotonate (5 g.) added dropwise with cooling to 6.07 g. Et methylaminoacetate during 15 min., the mixture kept overnight at room temperature, treated with Et2O, and distilled gave 4.3 g. Et N-ethoxycarbonylmethyl-γ-methylaminocrotonate (V), b0.1 95-6°. V (1.56 g.) in 15 cc. alc. shaken 1 hr. with H over PtO2 gave 0.2 g. Et N-ethoxycarbonylmethyl-γ-methylaminobutyrate (VI), b10 134-5°. The alc. distillate contained Et butyrate. A similar result was obtained in attempts to effect the hydrogenation in the presence of Pd-C. VI (by Dieckmann cyclization, followed by acid hydrolysis and decarboxylation) afforded 1-methyl-3-oxopiperidine, b11 56-8°; MeI derivative, prisms, m. 200-2° (decomposition). MeNH2 and acrylonitrile gave β-(methylamino)propionitrile. Alcoholysis gave Et β-(methylamino) propionate. The ester (17.4 g.) and 11.1 g. Et bromoacetate kept overnight at room temperature gave N-(β-ethoxycarbonyl-ethyl)-N-ethoxycarbonylmethylmethylaniline (VII), b0.15 74°. Cyclization of VII gave 1-methyl-3-oxopyrrolidine, b21 48-9°; methiodide m. 234° (decomposition). Na salt of 2-hydroxymethylenetropinone (2 g.) heated 10 min. in 10 cc. AcOH with 1.1

g. PhNHMe gave 1.4 g. 2-(methylanilinomethylene)tropinone (VIII), rhombic prisms, m. 121-2° (Me2CO). Attempts to reduce VIII to 2-(methylanilinomethylene)tropine or 2-(methylanilinomethylene)tropine under a variety of conditions were unsuccessful. Dehydration of tropine with AcOH-H2SO4 gave tropidine (IX). Trifluoroacetic anhydride (40 g.), obtained by dehydrating the acid with P2O5, added dropwise during 15 min. to 5.6 g. 86% H2O in 83 cc. CH2Cl2, the mixture stirred 15 min. at 0°, dried 0.5 hr., and filtered gave trifluoroacetic acid (X). IX (5 g.) added to 9.45 g. CF3CO2H in 33 cc. MeCN, then X added (10 min.), the mixture kept 4 days at 0°, the solvents removed, the oil dissolved in 30 cc. CH2Cl2, the solution treated with 5 g. anhydrous Na2SO4 then 30 g. K2CO3, stirring continued 4 hrs., the solution decanted, the residue washed with CH2Cl2, and evaporated gave 4.86 g. brown oil. Fractionation in vacuo gave 0.3 g. IX, followed by 1.63 g. 2β,3β-epoxytropine (XI), b6 93-4°. Attempts to liberate XI from its salt by use of NEt3 or Amberlite were unsuccessful. XI picrate m. 255° (decomposition). Attempts to prepare XI by treatment of IX or tropidine trifluoroacetate with X in the presence of anhydrous Na2CO3 gave IX N-oxide; picrate, yellow needles, m. 255-6.5° (decomposition). Reduction of the oxide with SO2 gave IX and on catalytic reduction gave tropine; picrate m. 285°. The action of HCO3H on IX formate gave principally the unchanged base, accompanied by a little 2β,3α-tropine-diol (XII). XI (2.08 g.) in 30 cc. Et2O added to 0.28 g. LiAlH4 in 30 cc. Et2O during 15 min., the mixture left 16 hrs. at room temperature, decomposed, the solution decanted, and distilled gave 1.62 g. (±)-2-β-tropanol (XIII), b18 94-5°; picrate m. 263-3.5° (decomposition). Attempts to oxidize XIII to (±)-isomer of I with CrO3 were unsuccessful. In one or two expts., a small yield of crystalline material was obtained, m. 140°. Hydrolysis with NaOMe in MeOH 2 days at room temperature gave XII. It was concluded that the product was either 2β-acetoxy-3α-tropanol or 3α-acetoxy-2β-tropanol. In one experiment, IX was detected in the product. (CF3CO)2O (6.3 g.) added during 10 min. to 1 g. 86% H2O2 in 40 cc. CH2Cl2, the mixture stirred 15 min. at 0°, the solution added during 10 min. to IX trifluoroacetate (from 2.5 g. IX) in 20 cc. MeCN, the mixture refluxed 0.5 hr., set aside overnight, evaporated, the sirup dissolved in H2O, saturated with K2CO3, and extracted 24 hrs. with Et2O gave 1.3 g. XII, rhombic prisms, m. 101°; MeI salt, prisms, m. above 320°; picrate, yellow needles, 208-10° (decomposition). Attempts to dehydrate XII with 20% H2SO4 or KHSO4 resulted in recovery of XII. XII (1.93 g.) with 0.7 cc. AcOH and 1.5 cc. concentrated H2SO4 heated 5 hrs. at 165° gave 1.52 g. (±)-2β,3α-tropine-diol (XIV), m. 103.5-5.0° (ligroine). A small yield of tropinone was also obtained; picrate m. 219°. SOCl2 (2 cc.) added dropwise to 0.61 g. XIV, the mixture stirred 0.5 hr. at room temperature, refluxed 18 hrs., and extracted with Et2O-CH2Cl2 gave 0.33 g. 3-chlorotropidine, b0.1 52-4°. IX (5 g.) in 50 cc. H2O at 0° treated with 4.35 g. KMnO4 and 8.7 g. MgSO4.7H2O in 435 cc. H2O during 5 hrs., stirred 1 hr., cooled, extracted 30 hrs. with Et2O in the presence of 500 g. KOH, and the extract concentrated gave unchanged IX. The remaining oil extracted with ligroine and evaporated gave 0.40 g. XIV; picrate, yellow rhombs, m. 239.5-40.5° (decomposition). IX (0.47 g.) in 10 cc. Et2O left 2 days at room temperature with 1

g. OsO₄ in 20 cc. Et₂O, the osmic ester collected, dissolved in 50 cc. H₂O, refluxed 0.5 hr. with 6 g. Na₂SO₃ in H₂O, saturated with K₂CO₃, and extracted 48 hrs. with Et₂O gave 0.5 g. XIV. XIV (0.36 g.) heated 6 hrs. at 120° with 3 cc. concentrated H₂SO₄ gave 0.18 g. tropinone, b₁₈ 104°; picrate m. 219°. Isovaleronitrile (by refluxing isobutyl bromide, KCN, and 60% alc.) (20 g.) refluxed 45 min. with 350 cc. alc. during addition of 33 g. Na, acidified, evaporated, the residual aqueous solution basified, and extracted gave 14 g. residual isopentylamine, b. 96-7°. Isopentylurethan, prepared by condensation of the amine and ClCO₂Et in quant. yield, b₁₄ 106-7°. The urethan (40 g.), 100 cc. Et₂O, 100 g. NaNO₂, 30 g. ice, and 140 cc. H₂O mixed and shaken 1 hr. below 15°, accompanied by the addition of 66 cc. concentrated HNO₃ and 100 cc. H₂O, gave 46 g. isopentyl-N-nitrosourethan (XV). Cyclohexanone (25.5 g.), 30 cc. MeOH, and 0.6 g. anhydrous Na₂CO₃ treated during 1.5 hrs. with 46 g. XV and after 16 hrs. at room temperature distilled gave 27.3 g. product, b₁₃₋₁₄ 102-6°, purified by formation of 2-isobutylcycloheptanone semicarbazone (XVI), plates, m. 131-2° (50% aqueous MeOH). Hydrolysis of XVI by heating with aqueous (CO₂H)₂ furnished 16.5 g. 2-isobutylcycloheptanone (XVII), b₁₂₋₁₃ 104-5°; 2,4-dinitrophenylhydrazone, plates, m. 76°. XVII (15 g.) in 20 cc. MeOH mixed with NH₂OH·AcOH in MeOH, the mixture refluxed 0.5 hr., evaporated, and the oil taken up in Et₂O gave 14.6 g. 2-isobutylcycloheptanone oxime (XVIII), b₁₁₋₁₂ 140-1°. XVIII (6.8 g.) in 100 cc. Et₂O added during 0.5 hr. to 2.5 g. LiAlH₄ in 150 cc. Et₂O, after 24 hrs. at room temperature the solution refluxed 3 hrs., cooled, decomposed, and fractionated gave 5.1 g. 2-isobutylcycloheptylamine (XIX), b₁₅ 124°. XIX (2 g.), 3 g. 90% HCO₂H, and 3 g. 40% HCHO mixed in the cold, heated 3 hrs., 15 cc. dilute HCl added, and the mixture extracted with Et₂O gave 2 g. II, b₁₅ 114°; MeI derivative, softening at 85°, m. 102-5°. Infrared spectra were given for a number of the above compds.

L7 ANSWER 5 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1960:10940 CAPLUS
DOCUMENT NUMBER: 54:10940
ORIGINAL REFERENCE NO.: 54:2158f-i,2159a-i,2160a-f
TITLE: Reductones. XII. The synthesis of acetoacetic ester-1-C₁₄ and α,β -dioxobutyric acid ester-1-C₁₄
AUTHOR(S): Dahn, H.; Hauth, H.
CORPORATE SOURCE: Univ. Basel, Switz.
SOURCE: Helvetica Chimica Acta (1959), 42, 1214-24
CODEN: HCACAV; ISSN: 0018-019X
DOCUMENT TYPE: Journal
LANGUAGE: German

AB cf. C.A. 52, 13717g. Ethyl acetoacetate-1-C₁₄ (I) was prepared in two ways: MeCN + BrCH₂C₁₄O₂Et (II) + Zn → I-1-C₁₄ in 46% yield, 99.5% of the activity remaining in the 1-position; and AcCl + CH₂(C₁₄O₂Et)(CO₂R) → AcCH(C₁₄O₂Et)(CO₂R), where R = CHMe₂ or CH₂Ph, and the CO₂R group removed to produce I-1-C₁₄. The reaction of I-1-C₁₄ with HNO₂ to give the 2-isonitroso compound, which was decomposed by N₂O₄, yielded AcCOC₁₄O₂Et (III). Mol. wts. indicated that the hemihydrate of III was a dimer, and although the ultraviolet data showed two CO groups, indicating an open chain 1-3 diol, the pH depression by HBO₃ suggested a cyclic, cis-1,2-diol. Thus, BrCH₂CO₂H-1-C₁₄ (1 mc./millimole) was esterified with

diazoethane in ether and the crude II-1-C14 diluted with inactive ester. Etched and dried Zn wool (15.5 g.) was stirred and heated 75 min. with 20 g. diluted II-1-C14, 31.1 ml. dry MeCN, 20 ml. absolute C₆H₆, and 10 ml.

absolute

ether. The solution was heated an addnl. 2.5 hrs. under reflux, cooled, 80 ml. ice-cold 2N H₂SO₄ added, the organic phase separated, washed with water and 2N NaHCO₃, dried, and distilled on the water bath. Distillation of the residue gave 71.4 g. I-1-C14, b₁₀ 66-8°, average sp. mol. BaCO₃ activity after dilution with 11.88 g. inactive I $4.948 \pm 0.035 + 105$. I-1-C14 was decarboxylated with EtOH and 2N H₂SO₄ 1.5 hrs. at 80° and the CO₂ absorbed as BaCO₃, sp. mol. activity $4.926 \pm 0.023 + 105$, indicating 98.7% retention of activity in the carboxyl group. I-1-C14 (120.2 mg.) in 0.5 ml. EtOH and 4 ml. 2N H₂SO₄ was decarboxylated 2.5 hrs. at 80°, cooled, neutralized with 4 ml. 2N NaOH, and 124 mg. semicarbazide-HCl and 189 mg. Na acetate-3H₂O added. After 5 hrs. the product was dried at 25°C in vacuo. The residue was extracted with MeOH, evaporated, and crystallized from water to yield 82 mg. crystals, m. 186-8°, of acetone semicarbazone. The sp. mol activity was $0.033 + 105$ and after two more crysts. was $0.018 + 105$. A solution of 34.8 ml. dry Et acetate, 20 g. II, 20 ml. absolute benzene, and 10 ml. absolute ether was added dropwise during 1.5 hrs. with heating and rapid stirring to 15.5 g. Zn wool, then heated 4 hrs. under reflux, and finally cooled in ice, and 75 ml. 2N H₂SO₄ added. After treating as above, 4.31 g. I (28% yield), b₁₀ 66-8°, was obtained. The yield of I was less if the Zn-II compound was prepared first (7%) or if II was added to the mixture of Et acetate and Zn (16%), or if AcOH was used instead of H₂SO₄ (19%). Control reactions showed that Zn and Et acetate alone produced only 3% I. A solution of 51.8 ml. PhCH₂OH in 40.4 ml. absolute pyridine was added during 2 hrs. at 20° with stirring to 37.8 ml. ClCH₂COCl, then heated 2 addnl. hrs., the mixture extracted with water and ether, the ether layer washed with 2N

H₂SO₄

and 2N NaHCO₃, dried, and distilled to give 87.7 g. ClCH₂CO₂CH₂Ph (IV), b_{0.4} 84-6°, n_{22D} 1.5220. NCCH₂CO₂Et (15 ml.) and 75 ml. PhCH₂OH heated 2 hrs. at 195-205° and the alcs. removed in vacuo gave 28.8 g. NCCH₂CO₂CH₂Ph (V), b_{0.02} 95°, n_{25D} 1.5173, nitrile band at 4.44 μ , ester band at 5.73 μ , and C:C band at 6.24 μ (liquid film). V could not be obtained from IV and KCN. V (22.6 g.) in 7.52 ml. absolute EtOH treated with dry HCl 4 hrs. at 0°, allowed to crystallize 36 hrs. at -5°, filtered, washed with ether and pentane, and dried gave 31.6 g. leaves, m. 88-90° (decomposition). The crystals were shaken 4 hrs. with ice water, neutralized with Na₂CO₃, and extracted with ether. Removal of the ether gave 71% ethyl benzyl ester of malonic acid (VI), b_{0.3} 110°, n_{26D} 1.4922, ester bands at 5.75 μ and C:C bands at 6.22 μ (liquid film). K (3.91 g.) was dissolved in 60 ml. absolute tert-BuOH and the excess tert-BuOH distilled VI (11.11 g.) in 20 ml. absolute ether was added and the mixture heated 15 min. under reflux. After addition of 30 ml. absolute ether, a solution of 14.2 ml. AcCl in 15 ml. absolute ether

was added

at 0° with stirring during 1 hr., the mixture stirred 2 hrs. at 22°, and finally heated 30 min. under reflux. The mixture was cooled, treated with ice water extracted with ether, the ether solution washed with 2N KHCO₃, dried, and distilled. The residual oil (VII) was dissolved in 75 ml. absolute Et acetate, 1.5 g. Pd-C added, and hydrogenated 35 min., 1.078 l. H being absorbed. The solution was filtered, the solvent evaporated, and the residue distilled in vacuo. The fraction, b₁₀ 60-100°, was dissolved in 20 ml. 0.5N absolute EtOH-HCl,

and allowed to stand 12 hrs. at 22°, and finally distilled first at atmospheric pressure, and then at 66-8°/10 mm. to yield 3.67 g. I. The crude VII was dissolved in ether, cooled, extracted rapidly with ice-cold N NaOH, and the ether solution washed with water. After drying and distillation

of

the ether the residual oil b0.1 147-9°, n_{25D} 1.5033, vinyl ester bands at 5.68 μ, ester bands at 5.82 μ, and C:C bands at 6.05 μ (liquid film), no longer showed the FeCl₃ reaction, and was identified as O-Ac derivative of enolacetylmalonic acid ethyl ester benzyl ester (VIII). Acidification of the NaOH extract, extraction with ether, and distillation at 80-95°/0.4 mm. gave (apparently) acetylmalonic acid ethyl ester benzyl ester, λ 3.1 to 4.2 μ (associated OH), 5.7-5.9 μ (ester), 6.12 μ (C:C), and 6.24 μ (phenyl) (liquid film), and a red FeCl₃ reaction. ClCH₂CO₂H tert-Bu ester (60.2 g.), 13.0 g. KCN in 160 ml. tert-BuOH, 25 ml. water, and a trace of NaI was heated 5 hrs. at 90°, then concentrated in vacuo, extracted with ether, the ether solution

washed

with water, 2N HCl, and 2N KHCO₃, and dried. Removal of ether and distillation in vacuo gave 18.6 g., b. 42-6°, and 4.3 g., b. 94.7°. The first fraction was redistd. at 86-8°/12 mm. to give 18.5 g. cyanoacetic acid tert-butyl ester (IX), d₂₁ 1.0095, n_{21D} 1.4172, b. 107-8, λ 4.40 μ (nitrile) and 5.74 μ (ester) (liquid film). The second fraction redistd. at 90-2° gave a colorless oil, n_{22D} 1.4312, recrystd. from MeOH-water to leaflets, m. 58-9°, λ (Nujol) 4.41 μ (nitrile) and 5.74 μ (ester), apparently cyanosuccinic acid di-tert-Bu ester. IX could not be prepared by alcoholysis of malonic acid ethyl tert-Bu ester, also, cyanoacetic acid Et ester did not react with tert-BuOH. K (3.91 g.) in 60 ml. absolute tert-BuOH and 10 ml. absolute ether was treated at 22° with 7.06 g. IX in 20 ml. absolute ether, then diluted with 100 ml. absolute ether, and

stirred at

-10° 2 hrs. with dropwise addition of 14.2 ml. acetyl chloride in 20 ml. absolute ether. Ice water was added, the ether phase separated, washed

with

water, and dried. Evaporation of the ether and distillation of the residue gave 1.25

g. cyanoacetoacetic acid tert-Bu ester (X), and 6.83 g. O-acetyl derivative of enol of cyanoacetoacetic acid tert-Bu ester (XI), b. 87-9°, d₂₄ 1.0657, n_{24D} 1.4542, λ 233 mμ (log ε 4.02) (EtOH), λ 4.49 μ (α,β-unsatd. nitrile), 5.60 μ (vinyl ester), 5.78 μ (α,β-unsatd. ester), and 6.14 μ (C:C) (liquid film). XI (5.72 g.) in 20 ml. acetone was treated with 15 ml. 2N KHCO₃ with gas evoln. After 2 hrs. shaking at 22° the solution was acidified, extracted with ether, washed, and distilled in vacuo to give 4.25 g. X, b0.2 57-9°, leaflets from pentane, m. 44-6°, λ 195 mμ (log ε 3.84) and 253.5 mμ (log ε 4.07) (EtOH), broad band at 3.5 μ, and bands at 4.51 μ, 6.05 μ (β-oxo ester, enolic), 6.22 μ (conjugated C:C) (CH₂Cl₂), red coloration with FeCl₃. I-1-C14 (17.08 g.) and 13.6 g. NaNO₂ treated dropwise during 45 min. with 50 ml. 4N H₂SO₄ at 0°, stirred 2 hrs., then diluted with 40 ml. water and extracted with ether, the ether phase washed with water and 2N NaHCO₃, and dried gave an ether solution of isonitrosoacetoacetic ester-1-C14 (XII). During 4 hrs. XII-1-C14 was treated with 11 ml. N₂O₄, the solution held overnight at 0°, and finally 2 days at 22° with warming and gas evolution. The ether was removed and the residue distilled to give 7.87 g. oil, which was dissolved in water, shaken with CaCO₃, and extracted with ether to give 5.69 g. III-1-C14, yellow oil, b10

64-6°, after three distns., sp. molar activity 4.908 ± 0.030 + 105. For comparison, inactive III b12 68°, n_{20D} 1.4135, λ 190 m μ (log ϵ 3.19) and 420 m μ (log ϵ 1.30) (cyclohexane), λ 5.72 μ and 5.78 μ (diketone) (CH₂Cl₂). III-1-C14 and 0.5 mole water crystallized from CHCl₃ and dried 15 hrs. at 22° over CaCl₂ gave needles, m. 94-5°. Mol. weight detns. in camphor and Exalton gave values of 230, in acetone 226. III-1-C14 had in water λ 188 m μ (log ϵ 3.39), 219 m μ (log ϵ 2.63), 288 m μ (log ϵ 2.00), in EtOH λ 195 m μ (log ϵ 3.18), 221.5 m μ (log ϵ 2.61), 289 m μ (log ϵ 1.98), in CH₂Cl₂ λ 2.84 μ (OH), 5.75 μ (C:O), in Nujol λ 2.83 and 3.01 μ (associated OH) and 5.72, 5.76 and 5.82 μ (C:O functions). Direct oxidation of I with SeO₂ in boiling dioxane yielded 29% crude III. I in Ac₂O with gaseous N₂O₃ at 20° gave 11% III, with liquid N₂O₄ at 20° 17% III. Pure XII in ether, with N₂O₃ at 20° gave 11% III, with N₂O₄ 28% III. XII with HCHO-HCl at 20° gave 17% III. α -Hydroxyacetoacetic ester, b12 93-6°, n_{19D} 1.4340, red FeCl₃ test in EtOH, decolorized dichlorophenol-indophenol immediately and was oxidized with a slight excess of FeCl₃ in water at 20° to give 30% III. III (72 mg.) in 3 ml. water was treated with 60 mg. o-phenylene-diamine in 1.5 ml. EtOH and heated to 100° 5 min. with the addition of one drop 2N HCl. On cooling, 102 mg. needles, m. 73-3.5°, of 3-methylquinoxazoline-2-carboxylic acid ethyl ester separated For C14 determination the labeled substance in weighed portions, corresponding to 30 mg. BaCO₃, was oxidized with CrO₃ to CO₂, converted to BaCO₃, and filtered. The dry BaCO₃ layer was smoothed with a polished steel die and counted directly.

L7 ANSWER 6 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 1954:51432 CAPLUS
 DOCUMENT NUMBER: 48:51432
 ORIGINAL REFERENCE NO.: 48:9107h-i,9108a-b
 TITLE: Oil-modified alkyd resins
 INVENTOR(S): Gourley, Samuel; Purvis, John E. B.
 PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 697318		19530923	GB 1950-6343	19500314

AB In the manufacture of oil-modified alkyd resins, catalytic Ca salts of fatty acids are precipitated in fine dispersion during esterification and produce a haze. By addition of dibasic acids, the precipitate is flocculated and can be removed to produce a clear haze-free product. Dibasic acids such as oxalic, malonic, succinic, adipic, or sebacic acid are used to precipitate the Ca salts. For example, 3000 parts of alkali-refined linseed oil (I) is heated to 240° with stirring under CO₂. In 90 min., 534 parts of pentaerythritol (II) containing Ca formate equivalent to 0.1% CaO is added. The mixture is maintained at 240° during these addns. and for 4 1/2 hrs. more. The II melts and reacts with I forming a homogeneous liquid consisting mainly of an ester. The fatty acid radical

of I esterifies one OH group of the glycerol and the II. The product is cooled to 90-95° and 2.9 parts H₂C₂O₄ are added to give a flocculent precipitate. When alcoholysis is substantially complete, 1107 parts of C₆H₄(CO)₂O and 102 parts of II with the same Ca formate content as before are added. The mixture is heated to 200° until its acid value falls to < 10. The resulting melt is perfectly clear and free from haze. Another formula contains 2750 g. of I and 870 g. of glycerol with 2.5 g. of Ca(OAc)₂. Phthalic acid or its anhydride, with or without maleic anhydride, are used for esterification of an incompletely esterified polyhydric alc. composition prepared by alcoholysis of a fatty oil with one or more polyhydric alcs. With sebacic acid, the cooled alcoholysis product is centrifuged before esterification with phthalic anhydride.

L7 ANSWER 7 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1952:28420 CAPLUS
 DOCUMENT NUMBER: 46:28420
 ORIGINAL REFERENCE NO.: 46:4813c-f
 TITLE: Synthetic drying oils
 PATENT ASSIGNEE(S): N. V. de Bataafsche Petroleum Maatschappij
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 68954		19511115	NL	

AB Polymers of allyl-type alcs. (I), which are prepared from polymeric esters of allyl alcs. or these polymeric esters (II) themselves are brought into reaction with unsatd. fatty acids (III), their anhydrides or halides (cf. Dutch patent 68,281). I may be prepared from II by hydrolysis in the presence of a Cu compound as a catalyst or by alcoholysis preferably with the same allyl-type alc. as is present in the polymer, since such a selection enables a monomeric ester, which may be directly subjected to polymerization, to be recovered. I may consist of one or more kinds of allyl alcs. while representatives of I containing 3 to 10 monomer units are preferred. Instead of the raw polymers there may be used polymers which are air-blown, hydrogenated, or treated with SO₂. It is advantageous to use III with at least 16 C atoms and a iodine number (Wijs) of at least 120, such as palmitoleic, linolenic, arachidonic, clupadonic, licanic acids, etc. The acids may be prepared by isomerization, dehydration, dehydrogenation, or synthesis, or may be obtained from natural oils, tall oil, or waxes. The reaction between I and III may be carried out in solution, preferably in the presence of a catalyst, with continuous removal of H₂O and under a blanket of an inert gas. The drying oils obtained, which may be purified, decolorized by a treatment with acid or alkali, bleached and bodied by heating, preferably in the presence of O at a temperature between 38 and 260°, are preferably used in the presence of 0.01 to 1.0% by weight of a usual drier. Drying is also promoted by O-liberating compds. The oils, which are color-stable at room temperature, may be used in the manufacture of paint and lacquer, and for sizing, resp., impregnating fibrous material. In an example, 9 parts of polyethyl alloxy formate were heated with 14 parts linseed fatty acids at 270° for 10 min. and at 300° for 30 min. A pale yellow drying oil having an acid number of 57 was obtained.

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L7 ANSWER 8 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1949:45539 CAPLUS
 DOCUMENT NUMBER: 43:45539
 ORIGINAL REFERENCE NO.: 43:8210d-i,8211a-f
 TITLE: Organic cyclic silicon condensation polymers
 INVENTOR(S): Hersh, Joseph M.
 PATENT ASSIGNEE(S): Continental Oil Co.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2464231		19490315	US 1945-600239	19450618

GI For diagram(s), see printed CA Issue.
 AB Monomeric cyclic silicon compds. have been condensed to form cyclic silicon condensation polymers (I) by improved methods and the resulting polymers used in numerous compns. I may be prepared from silicon dihalides or disilicon halides. E.g. CH₂.CH₂.CH₂.CH₂.CH₂.SiCl₂ (II) is prepared by stirring in a reaction flask with a reflux condenser 2.5 mols. Mg chips and 5-10 vols. anhydrous ether (on the halide used) and adding 1 mol. 1,5-dibromopentane at first slowly and undild., then more rapidly with anhydrous ether diluent. The reaction may require warming to start, or the addition of a reaction promoter, such as iodine or EtI. During the reaction an even ether reflux should be maintained for 3 hrs. by cooling. To the Grignard compound which seps. as an oily bottom layer is added slowly with rapid stirring and sharp cooling 1 mol. SiCl₄ in ether solution, the reaction product is decanted from the solids and fractionally distilled; essentially pure II is collected at 165-175°. The hydrolysis of II to the primary cyclic silicone (III) where n is not more than 5 is carried out by dissolving II in 2-3 vols. C₆H₆, adding gradually to ice-water or ice-brine, extracting with C₆H₆ and vacuum distillation of the solvent. III may be further condensed by dissolving in a noncondensable hydrocarbon solvent and treating with an acid-acting chemical condensing agent (IV), such as H₂SO₄, HSO₃Cl, HSO₃F, H₃PO₄, H₄P₂O₇, HPO₃, P₂O₅, P₂S₅, PCl₃, PCl₅, ZnCl₂, CoCl₂, MnCl₂, FeCl₃, AlCl₃, AlBr₃, HF, BF₃, or HI. The time of exposure of III to IV detcs. the degree of condensation. At the optimum polymeric structure the condensable mass is freed of IV and inhibited from further condensation by storage at low temps., or solution in a noncondensing hydrocarbon medium, or by the addition of a condensation inhibitor (V), such as EtOH, iso-PrNH₂, certain ethanolamines, Et silicate, Et borate, PhOH, p-NH₂C₆H₄OH, N-tert-butyl-p-aminophenol, Ph silicate, or Et acetate in amts. from 1 to 10%. V must be removed prior to use of the condensed III. Many monomeric cyclic silicon compds. are listed which will undergo the above reactions producing stable, homogeneous silicones of 500 to 10,000 mol. weight Disilicon halides may be prepared as follows: "chloro dicyclobutyl silico ether" (VI) is prepared by treating 1 mol. silicon oxychloride and 5 mols. Mg in anhydrous ether with 1,4-dichlorobutane to complete reaction, distilling off the ether and the crude VI. VI is not purified but is hydrolyzed rapidly in ice-water, washed to remove HCl producing primary dicyclobutyl silicol ether (VII) which has 2 hydroxyl

groups per mol. This may be further condensed to give the condensed dicyclic silicone. VII is a practically colorless, limpid liquid which, over concentrated H₂SO₄, gradually condenses giving off H₂O, to form a more highly condensed cyclobutyl silicone. Direct preparation of polymeric cyclic silicones may be carried out by using active metals, such as Mg, Zn, Al, Na, Li, K, Li-Na alloy, or Na-K alloy. Thus p-dichlorobenzene in the presence of molten dispersed particles of metallic Na (10 molal parts) in toluene or xylene reacts instantaneously with silicon oxychloride to produce "chloro dicyclophenyl silicol ether" which may then be hydrolyzed in the same vessel to produce I. Cyclic silicon esters (VIII) may be prepared by alcoholysis of the corresponding halogenated compds., such as VI. VIII are not readily hydrolyzed by H₂O and may be stored for considerable periods of time. Before condensation VIII is treated with constant-boiling H₂O to produce a controlled condensate. Many uses are described for the polymers. The compds. (I) may be used as untifoam agents in blended heavy-duty oils, as antifrothing agents in oily-organic processing systems, such as vacuum distillation of lubricating-oil stocks, dehydration of oils, and soap formation in the neutralization of fatty and organic acids. In certain lubricating compns. concns. of the condensed cyclic silicones of 0.1-10% may act as viscosity-improving and stabilizing agents. Halogen-bearing silicones have excellent extreme-pressure and load-carrying properties in these lubricants. When addnl. quantities of halogens are introduced in the cyclic silicon compound structure the resulting compds. form an extremely viscous, tough, thermotropic composition of high resistance to ignition and attack by insects or fungi; they are useful as fire-proofing, fungus- and insect-proofing components of impregnating or coating baths for fabrics, ropes, organic plastics, wood, etc. The higher polymeric forms of I are useful for elec. insulation, coating, etc.

L7 ANSWER 9 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1949:36595 CAPLUS
 DOCUMENT NUMBER: 43:36595
 ORIGINAL REFERENCE NO.: 43:6627f-i,6628a-i,6629a-i,6630a-i,6631a
 TITLE: Condensation reactions of N-substituted pyridones
 AUTHOR(S): Adams, Roger; Schrecker, Anthony W.
 SOURCE: Journal of the American Chemical Society (1949), 71, 1186-95
 CODEN: JACSAT; ISSN: 0002-7863
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 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 43:36595

AB The activity of the 6-Me group in 1-substituted 2-pyridones was studied as an aid in the synthesis of cytosine. Carbethoxymethyl groups gave compds. similar to β -keto esters and cyanomethyl groups compds. similar to β -carbonylated nitriles. These compds. formed Na enolates reacting with acyl and alkyl halides (cf. Kaslow and Cook, C.A. 40, 871.2). 2-Amino-6-methylpyridine (I) (108 g.) in 111 cc. H₂SO₄ and 830 cc. H₂O was diazotized with 73 g. NaNO₂ in 140 g. H₂O at 5°, stirred 1 h. below 10°, then heated to 90°, 205 g. K₂CO₃ added, the mixture evaporated on the steam bath, and the residue extracted with boiling C₆H₆, concentrated to 500 cc., and cooled to give 101 g. 6-methyl-2(1H)-pyridone (II), m. 158-9°, b. 282°. Boiling diazotized I (108 g.) was neutralized with Ba(OH)2.8H₂O 568 in boiling H₂O 1500 g., 50 cc. 25% NaOH added, and the filtrate concentrated to dryness; crystallization from 95% EtOH gave

115.5 g. of the Na derivative of 6-methyl-R (R = 2(1H)-pyridone throughout this abstract), m. 290°, very soluble in H₂O, insol. in Et₂O. To 98.7 g. II and 21 g. Na in 250 cc. warm MeOH, 130 g. Me₂SO₄ was added during 15 min. at room temperature; after 2 h.' refluxing, addition of 220 g. 25% aqueous NaOH, steam distillation to remove the byproduct 2-methoxy-R, filtration, and CHCl₃ extraction gave 82 g. 1,6-dimethyl-R (III), b₂ 110°, m. 56.5-8° (from dry Et₂O). Alkaline hydrolysis of the product from MeI and I gave only 23% III, and 2-picoline with Me₂SO₄, then alkaline ferricyanide, gave no III. III and dry HCl in Et₂O gave the HCl salt, m. 202-3° (corrected) (from absolute EtOH), sublimes at 75° and 3 mm.; III picrate, m. 134-6° (from 95% EtOH). 4-Methyl-R (IV), prepared as II in 78% yield, with extraction by boiling EtOH, b₁₂ 186-7°, m. 130° (corrected) (from C₆H₆). 1,4-Dimethyl-R (V), prepared as III in 77% yield, b₁ 110°, m. 59°, somewhat deliquescent but less so than III. V.HCl, prepared in absolute EtOH with dry HCl, cooling, and addition of dry Et₂O, m. 173-4°; V picrate m. 168-9°. Absolute EtOH (69 cc.) was cautiously added to 10.55 g. K covered with 60 cc. Et₂O, the mixture refluxed to dissolve K, 39.5 g. anhydrous Et₂C₂O₄ in 250 cc. Et₂O added at room temperature, then after 10 min. 30.75 g. III with shaking. After 3 days the precipitated yellow K salt (VI) of VII (see below) was crystallized from absolute EtOH, m. 310-20° (decomposition), 94.7% yield. Crude VI (61.8 g.) in 27 g. H₂SO₄, and 450 g. H₂O gave 42.8 g. Et 1-methyl-R-6-pyruvate (VII), m. 175-6° (from 95% EtOH). NaOEt prepared from NaH in Et₂O and EtOH with the above procedure gave 95% VI and then 85% VII. This procedure gave no pyruvic esters with 2-picoline, II, or 2-acetamido-6-methylpyridine. Similarly 84% K salt (VIII) of IX was prepared; stirring 12 g. VIII in 5.25 g. H₂SO₄, 55 g. H₂O, 30 g. chopped ice, and 100 cc. CHCl₃, extraction with 50 cc. more CHCl₃, addition of 3.5 cc. 28% NH₄OH in 30 cc. H₂O, further CHCl₃ extraction, concentration of the extract to 49 cc., and addition of 200 cc. ligroin (b. 30-60°) gave 8.1 g. (79%) Et 1-methyl-R-4-pyruvate (IX), m. 157-8° (from Me₂CO). Only 56% IX was obtained from VIII by the method used with VI. NaOEt condensation gave 65% IX. VII (2.23 g.) in boiling 22.3 g. 6% H₂SO₄ 30 min. gave a precipitate which was filtered after several hrs. in the ice box and crystallized from H₂O to give 1.78 g. 1-methyl-R-6-pyruvic acid (X), m. 239-40° (effervescence); 1-methyl-R-4-pyruvic acid (XI), 55% yield, and crystallized from 50% HOAc, m. 246° (effervescence). Addition of 3.3 cc. 30% H₂O₂ and 5 cc. H₂O to 1.95 g. X in 18 cc. 10% NaOH solution below 0°, keeping 48 h. in the ice box, removing excess H₂O₂ with MnO₂, chilling 1 h., acidifying with concentrated HCl to Congo red, several min.'s boiling, and further cooling gave 1.46 g. 1-methyl-R-6-acetic acid (XII), m. 188° (effervescence) (from H₂O); XII heated at its m.p. gave CO₂ and III; picrate, m. 134-6°. VII (0.446 g.), 3.6 cc. 10% NaOH, 0.7 cc. 30% H₂O₂, and 2 g. ice, 14 h. in the ice box, addition of 0.3 cc. 30% H₂O₂, and 14 more hrs.' chilling, etc., gave 0.18 g. XII. 1-Methyl-R-4-acetic acid (59% from XI), m. 184° (effervescence). VI (10.4 g.), 92 g. ice, and 14 cc. 30% H₂O₂ were chilled 1.5 h., 1.8 g. NaOH in 10 cc. H₂O added, then, after 42 h.' chilling, MnO₂, etc., gave 3.55 g. (58%) 1-methyl-R-4-carboxylic acid, tan crystals, purified by boiling a Na₂CO₃ solution with Darco, acidifying, and crystallizing from HOAc, m. 260° (cf. 247-8° of Spath and Koller, C.A. 17, 2712). Direct distillation gave 1-methyl-R; HgCl₂ double salt, m. 127°. XII (0.55 g.), 14 cc. MeOH, and 0.5 cc. H₂SO₄ refluxed 2

h., addition of aqueous K₂CO₃, concentration of the CHCl₃ extract, and addition of ligroin (b. 30-60°) gave 0.46 g. Me ester, m. 102°. XII (17.6 g.), 50 cc. EtOH, and 6 cc. H₂SO₄ refluxed 2 h., addition of 50 cc. C₆H₆, slow distillation of the steam bath to 0.5 volume, then concentration in vacuo to 110 cc., addition of K₂CO₃, etc., gave 18.3 g. Et ester (XIIa), m. 100-1°. XIIa did not condense with ArCHO and piperidine, or with Et₂C₂O₄ and KOEt. VII (15 g.) and 15 g. H₂NOH.HCl in 75 cc. C₅H₅N and 75 cc. absolute EtOH refluxed 4 h., concentration in vacuo, and trituration of the residue with 75 cc. cold H₂O gave 13.8 g. Et 1-methyl- α -isonitroso-R-6- propionate (XIII), m. 198° (from 95% EtOH). XIII (8.91 g.) boiled in 45 cc. 2 N aqueous NaOH 80 min., cooled, and 9 cc. concentrated HCl added, gave 7.49 g. free acid (XIV), m. 182° (decomposition) (from 50% HOAc). XIV was also prepared in 91% yield by addition of 10.42 g. ice-cold H₂NOH.HCl in 20 g. H₂O to 19.5 g. X, 14.75 g. NaOH, and 60 g. H₂O at 0°, filtration after 43 h. at 30°, and precipitation with 33 cc. concentrated HCl at 5°. XIV (19.1 g.) heated over a free flame gave much CO₂, H₂O, and 12.5 g. 1-methyl-R-6-acetonitrile (XV), b₁ 168°, as a yellow oil; crystallization from C₆H₆-Et₂O and redistn. gave colorless needles, m. 95.5-6.5°. XV did not condense with Et₂CO₃, but with BzH and C₅H₅N or piperidine gave high yields of a yellow impure product, m. 260-2°; it could not be purified. XV in boiling dilute NaOH in EtOH 3 h. and acidification gave 86% XII. Addition of 0.69 g. XIIa, then 0.45 cc. PhCH₂Cl, to 0.084 g. Na in 2 cc. EtOH, 21 h.' refluxing, addition of 0.2 cc. PhCH₂Cl, 3 h.' refluxing (mixture now neutral), steam distillation, solution of the oil in the residue in Et₂O, washing with dilute aqueous Na₂CO₃, concentration to 3 cc., addition of 30 cc. ligroin (b. 30-60°), and chilling gave 0.62 g. 1-methyl- α -benzyl-R-6-acetate, m. 104-5° (from 35% EtOH). Saponification of 0.74 g. in 1.0 g. NaOH, 2 g. H₂O, and 5 g. EtOH, with 2 h.' refluxing, and precipitation with dilute HCl gave 0.59 g.; decolorizing with Darco in dilute NH₄OH and repptn. gave the free acid (XVI), m. 155°. XVI heated in vacuo gave off CO₂ at 150°, then heated at 180° 5 min., and distilled at 150° and 2 mm. it gave 1-methyl-6-phenethyl-R, m. 95.5-6.5°. XV (1.48 g.) and PhCH₂Cl, etc., added (with 10 cc. C₆H₆) to NaOEt, extraction of the C₆H₆ layer with H₂O, filtration through Darco, and addition of ligroin gave 1.0 g. 1-methyl- α -benzyl-R-6-acetonitrile, m. 132° (from dilute EtOH, then C₆H₆-Et₂O); hydrolysis in 62% H₂SO₄ or preferably with KOH in EtOH-H₂O gave XVI. Addition of 4.30 g. XIIa, then 3.5 cc. BuI, to 0.51 g. Na in 10 cc. EtOH, 24 h.' refluxing, concentration to dryness, addition of 20 cc. H₂O, and Et₂O extraction gave 3.6 g. Et 1-methyl- α -butyl-R-6-acetate (XVII), b₂ 159-60°, n_D²⁰ 1.5180; the pale yellow oil gave colorless crystals in Dry Ice-Me₂CO. Lower yields were obtained from BuBr. XVII (0.59 g.) and 33% aqueous NaOH (0.93 g.) were heated on the hot plate to give a solution, then 1 h. on the steam bath, diluted with 1 cc. H₂O, 0.7 cc. concentrated HCl added at 0°, and the CHCl₃ solution of the precipitated oil washed with H₂O and concentrated; the residue gave CO₂ at 150°, and, after 5 min. at 180°, was distilled below 1 mm. and

at 90° as 6-amyl-1-methyl-R, nD₂₀ 1.5250. Addition of 2.52 g. XIIa to NaOEt (from 0.31 g. NaH, 0.77 cc. EtOH, and 20 cc. Et₂O), 15 min.'s refluxing, addition of 0.97 cc. AcCl in 10 cc. Et₂O at 0°, keeping 5 min. at 0° and 2 h. at 35°, extraction with aqueous NaHCO₃, and addition of ligroin (b. 30-60°) gave 1.16 g. crude liquid β-keto ester, solidifying at 6°. Refluxing 0.97 g. with 15 cc. concentrated HCl 22 h., concentration to a small volume, addition of excess saturated aqueous Na₂CO₃, concentration of the

CHCl₃ extract, trituration with ligroin, crystallization from C₆H₆, and distillation at 5 mm. and 150° bath temperature gave 0.18 g. 6-acetonyl-1-methyl-R, m. 136.5-7.5°; p-nitrophenylhydrazone, prepared by 30 min.'s refluxing in HOAc, m. 209-10° (blackening). III (2.1 g.), 2.58 g. 3-NO₂C₆H₄CHO, and 1.77 g. Ac₂O were heated 20 h. at 175-80°, the black oil treated 5 min. with boiling MeOH and 0.2 g. Norit, the MeOH removed by addition of 3 cc. concentrated HCl and 20 cc. H₂O and boiling,

the aqueous solution extracted with C₆H₆, boiled 2 min., made alkaline with aqueous 25% Na₂CO₃, and the precipitate repptd. from 2 cc. boiling EtOH with 30 cc. H₂O and crystallized from C₆H₆-ligroin, then 95% EtOH, as 0.05 g. 1-methyl-6-(m-nitrostyryl)-R, m. 216-18°. Refluxing 15.0 g. 2-acetamido-6-methylpyridine (Seide, J. Russ. Phys.-Chemical Society 50, 534(1918)), 10.6 g. BzH, and 5.1 g. Ac₂O 30 h., steam distillation, dilution of the residue with

250 cc. H₂O, acidification with HCl, filtration through Celite and Norit, and addition of NH₄OH gave a yellow oil; drying in Et₂O, precipitation from CHCl₃ solution with ligroin, solution in dilute HCl, and precipitation by addition of NH₄OH with chilling, and precipitation from EtOH with H₂O gave 2.94 g., crystallized from

C₆H₆-ligroin and from 70% EtOH, of 6-acetamido-2-stilbazole (XVIII), m. 149-50°. XVIII (4.2 g.) boiled 3 h. in 6 N HCl and crystallized from EtOH gave 3.98 g. 6-amino-2-stilbazole-HCl, m. 249-52°; addition of NH₄OH and crystallization from C₆H₆-ligroin (b. 90-110°) gave 96% free base (XIX), m. 110°. Addition of NaNO₂ to XIX in warm dilute H₂SO₄, 5 min.'s boiling, addition of excess NH₄OH, 2 min.'s boiling, solution of the precipitate in hot dilute aqueous NaOH, and buffering with CO₂ repptd. 48% 6-hydroxy-2-stilbazole (or 6-styryl-R), m. 210-11° (from 95% EtOH). 2-Acetamido-4-methylpyridine (8.0 g.) (cf. Seide, C.A. 18, 2896), 6.3 g. BzH, and 2.7 g. Ac₂O refluxed under N 46 h., addition of 15 cc. concentrated HCl, steam distillation of the dark oil, and extraction of the residue twice with 50 cc. boiling concentrated HCl gave a dark sticky residue (XX) and a clear yellow solution (XXI).

XXI was boiled 3 h., diluted with 50 cc. H₂O, boiled 4 h., cooled, the yellow flocculant precipitate dissolved in boiling EtOH, an excess of dilute NH₄OH added, the tan precipitate boiled in 50 cc. concentrated HCl with Norit, filtered hot, diluted with 50 cc. hot H₂O, then chilled 3 h., the precipitated product dissolved in 50 cc. hot EtOH, 4 cc. 28% NH₄OH in 10 cc. EtOH added, then hot H₂O to saturation, and the mixture chilled to give 1.52 g. 2-amino-4-stilbazole (XXII), m. 216-17° (from 95% EtOH). XX was digested with Me₂CO at

0°, then with boiling concentrated HCl, dissolved in 70 cc. boiling EtOH, and the solution heated with 40 cc. concentrated HCl; slow dilution with 100 cc. boiling H₂O gave a yellow precipitate, repptd. from boiling EtOH with NH₄OH as 0.29 g. microcrystals, m. 234-5°, containing C 84.26, H 5.59 and N 6.87%, but of unknown structure. XXII (2.4 g.) in 1.5 cc. concentrated H₂SO₄ and 10 cc. HOAc was chilled in ice-salt and precipitated as the sulfate; diazotization with gradual addition of 1.0 g. NaNO₂ in 2 g. H₂O at 0°, addition of more NaNO₂ at room temperature (to a pos. starch iodide test), precipitation with 100 cc. H₂O, addition of excess NH₄OH to the mixture at 90°, and crystallization from 95% EtOH gave 0.86 g. 2-hydroxy-4-stilbazole (or 4-styryl-R), m. 238-9°. Heating an intimate mixture of 42.5 g. II and 1.3 g. of the Na salt of II with 22.8 g. CH₂:CHCN on a steam bath 30 min. with shaking, addition of 1 cc. HOAc in 110 cc. boiling C₆H₆, and chilling the hot filtrate gave 52.5 g. 6-methyl-R-1-propionitrile (XXIII), m. 109-10° (from EtAc). Slightly lower yields resulted with 50% aqueous KOH, powdered NaOH, and Triton B (with dioxane) as catalysts. Pyrolysis of XXIII gave CH₂:CHCN and II easily. XXIII (18.4 g.), 92 cc. H₂O, and 6 cc. H₂SO₄ refluxed 3 h. and chilled gave 18.9 g. 6-methyl-R-1-propionic acid (XXIV), m. 165-6° (from H₂O, then Me₂CO). Esters of XXIV could not be prepared by alcoholysis of XXIII, or from II Na salt and BrCH₂CH₂CO₂Et, XXIV and EtOH-HCl, Ag salt of XXIV and MeI or EtI, II and CH₂:CHCO₂Et, or XXIV and CH₂N₂. The oily products always decomposed into acrylic ester and II when distilled, and treatment with K, KOEt, and NaH to remove ROH and give a pyridopicoline ring failed. Addition of 10.9 g. II, then 18 g. BrCH₂CO₂Et, to 2.3 g. Na in 50 cc. EtOH and 20 cc. C₆H₆, 2 h.' refluxing, concentration in vacuo to a small volume, addition of 100 cc. H₂O, and CHCl₃ extraction of the steam distillate gave 1 g. 2-(carbethoxymethoxy)-6-methylpyridine, b₁₅ 132°, n_D20 1.4909. Addition of 2 g. K₂CO₃ to the steam-distillation residue and continuous CHCl₃ extraction gave 13.7 g. Et 6-methyl-R-1-acetate (XXIVa), m. 81-2° [from C₆H₆-ligroin (b. 30-60°), then Me₂CO-ligroin]. Saponification of 1.24 g. with 7.4 cc. of boiling 35% aqueous KOH 30 min. and addition of 10 cc. H₂O and 5.7 cc. HCl gave 0.68 g. 6-methyl-R-1-acetic acid (XXV), m. 229° (effervescence) (from EtOH). XXV was also made in 21% yield from 2.18 g. II, 4.62 g. 50% aqueous KOH, and 1.98 g. ClCH₂CO₂H boiled 2 min. and 2 cc. H₂O added, with 3 min.'s boiling, cooling, solution in 7 cc. hot H₂O, addition of 1.8 cc. concentrated HCl, and chilling. Addition at 0° of 2.84 g. Et₂C₂O₄ to 0.76 g. K in 4.3 cc. EtOH and 9 cc. Et₂O, then after 10 min. 3.48 g. XXIVa, then C₆H₆ 15 and Et₂O 26 cc., and maintenance under a N atmospheric at room temperature 19 h. gave 2.42 g. red K salt; treatment with 0.5 cc. concentrated H₂SO₄ and 20 g. ice and crystallization from EtOH gave 1.61 g. Et 1-(carbethoxymethyl)-R-6-pyruvate, m. 137-8°. II (2.18 g.), 7.12 g. N-bromosuccinimide, and 0.25 g. Bz₂O₂ in 60 cc. boiling CCl₄ 30 min., hot filtration, concentration to dryness, and crystallization from 95% EtOH gave 1.2 g. 3,5-dibromo-6-methyl-R, m. and mixed m.p. 254-5°. Dropwise addition of 18.7 g. Br during 15 min. at 0° to 10.8 g. I in 47 g. 20% H₂SO₄, shaking 15 min. at room temperature, and addition to the colorless solution at 0° of 80 g. cold aqueous 20% NaOH gave 9.3 g. 2-amino-5-bromo-6-methylpyridine (XXVI), m. 83-4° [from ligroin (b. 90-110°)]. Addition of 32 g. Br below 35° to 10.8 g. I in 47 g. 20% H₂SO₄, 2 h.

on the steam bath, and chilling 16 h. gave 24.6 g. crude sulfate. Addition in small portions to 50 g. 10% aqueous NaOH at 0° and crystallization from 95% EtOH gave 17.15 g. 2-amino-3,5-dibromo-6-methylpyridine (XXVII), m. 144°. Diazotization of 8.4 g. XXVI in 20% H₂SO₄, dilution with H₂O, 5 min. on the steam bath, addition of 9 g. K₂CO₃ in 15 g. H₂O, and boiling, then chilling and crystallization from 95% EtOH and C₆H₆, gave 6.9 g. 5-bromo-6-methyl-R, m. 204°. Similarly prepared in 97% yield from XXVII, 3,5-dibromo-6-methyl-R m. 254-5° (from C₆H₆, then 95% EtOH) [cf. m.p. of 238-9° by Errera (Ber. 33, 2969(1900))].

L7 ANSWER 10 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1948:21270 CAPLUS

DOCUMENT NUMBER: 42:21270

ORIGINAL REFERENCE NO.: 42:4529b-i

TITLE: β-Propiolactone. V. Reaction with alcohols

AUTHOR(S): Gresham, T. L.; Jansen, J. E.; Shaver, F. W.; Gregory, J. T.; Beears, W. L.

CORPORATE SOURCE: B. F. Goodrich Research Center, Brecksville, O.

SOURCE: Journal of the American Chemical Society (1948), 70, 1004-6

CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

OTHER SOURCE(S): CASREACT 42:21270

GI For diagram(s), see printed CA Issue.

AB O.CH₂.CH₂.CO (I) (1 mole), added dropwise to 2 g. Na in 6 moles of the alc. (temperature maintained at 0°), gives the following HOCH₂CH₂CO₂R (yield of Me ester at 25° 76%, of Et ester 69% with 4 g. Me₃(PhCH₂)NOH): Yield, B.P.; R, %, °C., mm., n_D20, d₄20; Me, 85.1, 71, 13, 1.4225, 1.1153; Et, 80.1, 75, 8, 1.4222, 1.0545; Pr, 65.5, 98, 19, 1.4251, 1.0217; Bu, 77.2, 114, 20, 1.4284, 0.9989; C₈H₁₇, 64.5, 104, 4, 1.4392, 0.9484. The oily residue from the reaction with MeOH is Me β-(β-hydroxypropionyloxy) propionate, b₀.3 85-6°, n_D20 1.4429, d₄20 1.1902. With secondary alcs., it is more difficult to avoid the polymerization of I, probably because of the slower rate of the primary reaction. The noncatalyzed reaction of I with alcs. is extremely slow and ROCH₂CH₂CO₂H (II) and polymers are the only products. Some esterification of the alkoxy acids occurs, especially with the lower alcs. at higher temps. With secondary and tertiary alcs., these noncatalyzed reactions are still slower, more of I polymerizes, and no esters of the alkoxy acids are isolated. The acid-catalyzed reaction of I with alcs. is extremely complex. II and their esters, esters (III) of HOCH₂CH₂CO₂H, and polyester acids (IV) with terminal alkoxy groups are formed. The composition of the mixture obtained is dependent on the reaction conditions employed, the most important factors of which are the acid catalyst concentration, the temperature, time, and molar excess of alc.

Numerous

expts. are given (H₂SO₄ as catalyst) to show the effect of these factors. The quantity of III formed by the secondary reaction increases with time with a corresponding decrease of IV, and none of it formed in incomplete reactions. Polymerization, alcoholysis, and esterification are favored with increasing catalyst concentration and temperature. However, with

high acid

concentration only insol. polymers of higher mol. weight result. Decrease in

the

excess alc. favors the polymerization. The following consts. are reported: ROCH₂CH₂CO₂H; B.P.; R, °C, mm., n_D25, d₄20; Me, 102, 13,

1.4160, 1.0982; Et, 108, 10, 1.4178, 1.0450; Pr, 76, 1, 1.4204, 1.0043; iso-Pr, 70, 1, 1.4222, 1.0032; Bu, 72, 0.1, 1.4240, 0.9876; ROCH₂CH₂CO₂R; Me, 63, 40, 1.3993, 1.0052; Et, 60, 13, 1.4041, 0.9461; Pr, 87, 13, 1.4139, 0.9369; iso-Pr, 67, 13, 1.4059, 0.9150; Bu, 97, 6, 1.4190, 0.9109. The reaction with MeOH gives Me β -(β -methoxypropionyloxy) propionate, b_l.5 86°, n_D25 1.4260.

L7 ANSWER 11 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1943:37471 CAPLUS
DOCUMENT NUMBER: 37:37471
ORIGINAL REFERENCE NO.: 37:5968d-i,5969a-f
TITLE: An indole synthesis from a m-carboxyphenylhydrazone
AUTHOR(S): Koelsch, C. F.
SOURCE: Journal of Organic Chemistry (1943), 8, 295-9
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

GI For diagram(s), see printed CA Issue.

AB The conversion of lysergic acid (I) into isolysergic acid may be due to a shift of the double bond from the 2,3- into the 3,4-position involving the rings A, B, and C. An attempt is made to synthesize 1,3-dihydrobenz[cd]indole containing the A, B, C ring system, by the Fischer indole synthesis. m-Aminobenzoic acid (17.3 g.), in 10 cc. concentrated HCl and ice, is diazotized with 7 g. NaNO₂. When the solution is clear, 20 g. AcONa.3H₂O and 15.6 g. Et cyclopentanone-2-carboxylate is added, giving 2-carbethoxy-2-(m-carboxyphenylazo)cyclopentanone (II) as yellow needles which sinter at 105° and m. 118-20° (decomposition). II, when boiled with 7% Na₂CO₃ for 2 min. and acidified, gives 70% of the hydrazone m-HO₂CC₆H₄NHN:C(CO₂Et) CH₂CH₂CH₂CO₂H (III) as orange-brown crystals, m. 165-7°, which when boiled with absolute EtOH and H₂SO₄ gives the m-carbethoxyphenylhydrazone of di-Et α -ketoadipate, m. 125-7°. When boiled with 10% NaOH III gives the m-carboxyphenylhydrazone of α -ketoadipic acid, m. 215-18° (decomposition). When 165 g. III in 250 cc. absolute EtOH and 75 cc.

concentrated H₂SO₄ is boiled for 2 h. and, after addition of another 75 cc. H₂SO₄, for an addnl. 3 h., 2,6-dicarbethoxy-3-(2-carbethoxyethyl) indole (IV) and (NH₄)₂SO₄ crystallize on cooling. The latter is removed by washing with H₂O. The alc. mother liquor is diluted with H₂O and extracted with ether. The ether extract, after being washed with Na₂CO₃ and concentrated, gives a 2nd crop of

IV.

The ether mother liquor is evaporated to dryness and the residue redissolved in ether. Addition of petr. ether causes the separation of crude 2,4-dicarbethoxy-3-(2-carbethoxyethyl)indole (V). The acids obtained on acidification of the Na₂CO₃ extract, when boiled with EtOH in H₂SO₄ for 3 h., give some more V. IV (40-g. yield), recrystd. from EtOH, crystallizes with 0.5 mol. EtOH and m. 113°. V (58-g. yield) m. 105-6° after several crystns. from ether-ligroin. Oxidation of 5 g. IV in 25 cc. AcOH by slow addition of 4 g. CrO₃ in 13 cc. AcOH and 2 cc. H₂O at 25-30°, gives 4.6 g. Et β -(4-carbethoxy-2-ethoxalylaminobenzoyl)propionate (VI), m. 97-9°. Oxidation of V in the same way gives Et β -(6-carbethoxy-2-ethoxalylaminobenzoyl)propionate (VII), m. 84-6°. When VI is boiled with alkali, a yellow product, m. above 225°, probably 2,7-dicarboxy-4-hydroxy-3-quinolineacetic acid, is obtained. Alcoholysis of VI by boiling it for 3 h. with EtOH containing H₂SO₄ gives Et β -(2-amino-4-carbethoxybenzoyl) propionate (VIII),

bright yellow plates, m. 87-8°; Bz derivative, m. 86-8°, when boiled with aqueous NaOH gives a white crystalline acid, probably a quinoline derivative, which sinters and darkens at 210°. VII and EtOH containing H₂SO₄ give Et β -(6-carbethoxy-2-aminobenzoyl) propionate (IX) as a colorless basic oil. Diazotization of VIII and IX in H₂O or alc. gives only oily products. Diazotization of 4.5 g. VI in 25 cc. EtOH containing 2 cc. H₂SO₄ at 0° with BuONO gives the cinnoline (X), m. 168-71°. VII, under the same conditions, gives an oil which when boiled with 10% KOH gives β -(2-ethoxy-6-carboxybenzoyl)propionic acid, m. 166-8°. When VIII is boiled for 0.5 h. with 10% NaOH and the mixture acidified with H₂SO₄ to pH 3, β -(2-amino-4-carboxybenzoyl)propionic acid, bright yellow needles which do not m. 250°, is obtained. When immersed in a bath above 215°, it partially m., then resolidifies and becomes much lighter in color. IX under the same conditions gives β -(2-amino-6-carboxybenzoyl)propionic acid, flat tan needles, sinters 168° and m. 180° with gas evolution. From the mother liquor, 4-amino-1,3-diketo-2-hydrindeneacetic acid, sinters 192° and m. 202° with darkening, is obtained. It gives a deep red solution with Na₂CO₃ and a pale yellow solution with HCl.

L7 ANSWER 12 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1941:26771 CAPLUS

DOCUMENT NUMBER: 35:26771

ORIGINAL REFERENCE NO.: 35:4234g-i, 4235a-g

TITLE: The composition and source of the "esters" in distilled glycerol

AUTHOR(S): Tyutyunnikov, B.

SOURCE: Seifensieder-Zeitung (1941), 68, 57, 70-1, 82, 92, 103-4
CODEN: SSZTAW; ISSN: 0371-3296

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

AB Glycerol from the first condenser of a Van Ruymbeke still may contain Ca salts of higher fat acids, carried over by entrainment. Glycerol from the 2nd condenser may contain higher fat acid mono esters of glycerol which have distd: Both portions, especially the 2nd, may contain esters of caproic and higher acids. Under the usual analytical conditions, heating on the water bath with excess alkali for 15 min. is insufficient to saponify all of the esters. This may be due to the presence of lactones, etc., occurring in varying amts. The esters found in distilled glycerol are formed in the vapor state. Fat acids are set free from soaps by alcoholysis during distillation and are carried over in the steam if excess alkali is absent. A high content of salts of sulfonaphthenic acids may be present in saponification glycerol if the "Kontakt reagent" was made from kerosene. These acids during distillation of glycerol behave similarly to fat acids. Expts. showed that HOAc is distilled with glycerol from a glycerol solution of NaOAc. Formic acid under similar conditions appears in the distillate to a lesser extent. The weight of free alkali in the residue from distillation of sapon glycerol is much less than would be calculated from the weight and composition of the charge.

Corresponding

proportions of acids were formed during distillation Part of these came from the sulfonaphthalene salts. Aldehydes and acetates were practically absent from the distilled glycerol. Formic acid took an important part in the reactions. The aqueous distillate, when it contained free acids and

lactones, gave a pos. test for lactic acid. When the ether number was 0 or very small, the test for lactic acid was neg. Formic and lactic acids are not present in fats and are formed in industrial distillation of glycerol. At 280°, with excess of caustic alkali, glycerol yields propylene glycol, CH₃OH, HCOOH, (COOH)₂ and C₂H₅COOH. In absence of excess alkali, lactic acid is formed. With excess alkali, the lactic acid decomposes to CO₂, HCOOH, CH₃COOH and C₂H₅COOH. In absence of a large excess of alkali, lactic salts change to those of dilactylic acid. Similar reactions must occur during prolonged heating at 180° in the Van Ruymbeke still. The presence of formic and acetic acids in glycerol distillation residues can be explained thus: CH₂:CHCHO + H₂O → CH₂OHCH₂CHO; CH₂OHCH₂CHO + H₂O → H₂C(OH)₂ + CH₃CHO; H₂C(OH)₂ → HCHO + H₂O; 2HCHO + H₂O → HCOOH + CH₃OH; CH₃CHO + HCHO + H₂O → CH₃COOH + CH₃OH. The last equation occurs only to a very slight extent. Similar reactions may occur during hydrogenation in autoclaves. Acetaldehyde was found in some "sweet waters." No MeOH was found probably because of the difficulty of separation. The reactions suggest the method of formation of propylene glycol during distillation. The formation of lactates, dilactylates and formates also is explainable. They may be carried over by entrainment. Liquid recovered from the entrainment separators had sp. gr. 1.355 and ash content 5.5%. T. concludes: both lower and higher acids participate in ester formation. Salts of higher and lower fat acids, of lactic acid and lactides, when present in distilled glycerol are due to entrainment, which is also responsible for poor color. Formic acid is formed by reaction of acrolein and water vapor; also by reaction of glycerol and caustic alkali. The formation of lactic acid is due to the same reaction. Fat acids, from acetic upward, appearing in glycerol vapors are to be attributed to alcoholysis of their salts. The decrease in ester content of distilled glycerol by the introduction of excess alkali into the crude glycerol is to be attributed to the lessening of alcoholysis of soaps and the condensation of aldehydes into nonvolatile compds. The consumption of caustic alkali during distillation is to be explained by the reaction of the alkali with glycerol or with foreign substances present.

L7 ANSWER 13 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1937:44783 CAPLUS

DOCUMENT NUMBER: 31:44783

ORIGINAL REFERENCE NO.: 31:6244d-i,6245a-b

TITLE: Strychnine and brucine. XXXVI. Preliminary synthetical experiments

AUTHOR(S): Openshaw, H. T.; Robinson, Robert

SOURCE: Journal of the Chemical Society (1937) 941-6

CODEN: JC SOA9; ISSN: 0368-1769

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

GI For diagram(s), see printed CA Issue.

AB The object of the present expts. is to approach the strychnine skeleton as closely as may be in the hope that some degradation product may be synthesized. The preparation of Et 2-carbethoxycyclohexanone-2-β-propionate (IA) in 80% yield is described and also its hydrolysis with concentrated HCl to give 90% of cyclohexanone-2-β-propionic acid. The oily phenylhydrazone with boiling 20% H₂SO₄ gives the lactam of tetrahydrocarbazole-1-β-propionic acid (I), plates with a bluish tinge, m. 126° and tetrahydrocarbazolenine-11-β-propionic acid (II), m. 226°, the latter being soluble in dilute acids or alkalies. I was not reduced with H₂ and Pt, Sn and dilute EtOH-HCl or with Na and EtOH

or iso-AmOH; electrolytic reduction at a Pb cathode in AcOH-H₂SO₄ gives 1,9-trimethylenehexahydrocarbazole (III), m. 81-2°; addition of a trace of FeCl₃ to a solution in 5% HCl gives an intense red color. Dehydrogenation of III by Hg(OAc)₂ in AcOH or by heating with Pd-C gives 1,9-trimethylene-1,2,3,4-tetrahydrocarbazole, m. 87-8°; boiling Ehrlich's reagent gives a bluish green color, which fades to yellow on cooling. Reduction and acetylation of II yield N-acetylhexahydrocarbazole-11-β-propionic acid, m. 202°; in 60% H₂SO₄ it gives an intense reddish purple color with K₂Cr₂O₇, which fades rapidly through red to brownish yellow. Refluxing IA and EtOH-EtONa for 8 h. gives Et 6-carbethoxycyclohexanone-2-β-propionate, b₁₁ 189-90° (70% yield); FeCl₃ gives a deep violet color; this reaction is obviously alcoholysis and ring closure in a new position. With Na and ClCH₂CH₂CO₂Et in C₆H₆ there results 75% of Et 6-carbethoxycyclohexanone-2,6-β,β'-dipropionate (IV), b_{0.2} 182-3°; condensation in EtOH gives a poor yield of IV and a considerable quantity of Et heptane-1,3,7-tricarboxylate, b_{0.15} 147-8°; Na in C₆H₆ with a trace of EtOH and ClCH₂CH₂CO₂Et give 80% of IV. Hydrolysis of IV with concentrated HCl gives 98% of cyclohexanone-2,6-β,β'-dipropionic acid, m. 145°; Et ester, m. 60-1°; the orange, oily phenylhydrazone with EtOH-HCl, followed by reduction with Sn, yields the lactam. of hexahydrocarbazole-1,11-β,β'-dipropionic acid (V), m. 269-70°; K₂Cr₂O₇ in 60% H₂SO₄ gives a transient purple color, fading through rose-red to yellow.

L7 ANSWER 14 OF 14 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1906:152300 CAPLUS

DOCUMENT NUMBER: 0:152300

TITLE: On the Preparation of Pure Alkyl Malonic Ester.
[machine translation]

AUTHOR(S): Michael, A.

CORPORATE SOURCE: TUFTs Coll. Chem. Lab.

SOURCE: Journal fuer Praktische Chemie (Leipzig) (1905), 72,
537-54
From: Chem. Zentr., 1906, I, 745-747
CODEN: JPCEAO

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

AB [Machine Translation of Descriptors]. (See CONRAD, LIEBIG's Ann. vo. 204, pg. 134; Z. f. Phys. Ch. vo. 7, pg. 285; C. vo. 91, I. pg. 910; SCHEY, Rec. trav. Chim. Pays-Bas vo. 16, pg. 357; C. vo. 98, I. pg. 28; MICHAEL, Ber. German Chemistry Society vo. 38, pgs. 2091, 3217; C. vo. 1905, II. pgs. 396, 1665) the CONRAD method, effect of ethyl iodide on sodium malonic ester to alcoholic solution, supplies with the ethyl malonic ester contaminated by diethyl malonic ester. The proof of this non-uniformity is based on it that malonic ester of aqueous potash each concentration becomes fast into the potassium ethyl salt, the mono-alkyl malonic ester by diluted alkali analogous decomposing, against 25% Alkali however are rather stable, the dialkyl malonic ester of concentrated or also very much diluted alkali was only slowly saponified. With the help of this method, which is applicable both for the separation of these esters, and for the proof of their purity, in the CONRAD mono-ethyl malonic ester about 15% diethyl esters were proven, and due to the inadequacy a number on such compounds requires the parliamentary group method for the purification of such compounds based investigations of the repetition. Thus the formation goes from Butane-α, β, β-tricarbon ester from sodium ethyl malonic ester and chloroethyl acetate many more smoothly indicated before

itself, than of BISCHOFF and V. KUHLEBERG (Ber. German Chemistry Society vo. 23, pg. 638; C. vo. 90, I. pg. 752). For the easy production of more uniform Alkyl malonic ester, heating a mixture of potash powdered by sodium malonic ester and alcohol with a Alkyl halide and registering into a mixture are suitable malonic ester and an alkyl iodide; latter method is applicable also to alkylated acetoacetic acid. The increase of the ease of the saponifiability from dialkyl to Monoalkylmalonic ester and to malonic ester (methyl derivatives are more easily more saponifiable than ethyl and propyl derivatives) continues to stand in contradiction from E. FISCHER (Ber. German Chemistry Society vo. 31, pg. 3266; C. vo. 99, I. pg. 339; see also E. FISCHER and VAN'T HOFF, Ber. German Chemistry Society vo. 31, pg. 3277) set up statement, according to which the ability exerts a retarding influence on the saponifiability for salt formation of esters; with the alkaline. Hydrolysis attacks that alkali in the molecule, where most free negative energy is present, that is, here CO to the ester. If larger neutralization of the atoms of the carbonyl is caused (therefore conversion of free energy into bound) by a change of constitution, for example by introduction of the sodium to acetoacetic esters, then this means a relative protecting of the carbonyl against addition of the alkali, i.e. an aggravation of the hydrolysis. With the Natioacetoacetic ester also decomposes into aqueous solution after GOLDSCHMIDT and OSLAN (Ber. German Chemistry Society vo. 32, pg. 3392; C. vo. 1900, I. pgs. 171, 1070) only the small part of the ester of alkali, which is released into aqueous solution of the salt. Malonic ester neutralized Na far less than acetoacetic esters; here so much free positive energy comes to the metal that it under effect of water alcoholysis causes immediately, as the free energy of the metal changes by entrance into the carboxyl group well into bound energy and heat. The metal derivatives of the uric acid are well neutralized; those of the Tetramethyl uric acid, which are in fewer neutralized, are more easily decomposable by the relatively larger content of the CO group at free negative energy. The ease of the addition at the CO group indirectly atoms and their spatial position in the molecule affect strong; to it the slowing down of the hydrolysis of the dimethyl to the diethyl malonic ester and amide formation of the not substituted is to be led back over the monalkylated to dialkylated malonic ester; of E. FISCHER and DILTHEY (Ber. German Chemistry Society vo. 35, pg. 844; C. vo. 1902, I. pg. 745) set up theory does not explain these facts. Experimental part; Malonic acid; 1 part Potassium salt in 160 parts water does not give a precipitate with CaCl_2 . Diethyl ester. All over cyanogen acetic acid was prepared or available malonic ester contains N. for the removal of cyanogen ethyl acetate vibrates one raw malonic ester twice with diluted NH_3 ; its potassium compound develops from the ester and 50% igem potash, existed temporarily with presence of water, is crystalline and turns with water rapidly into alcohol and Potassium ethylmalonate. This develops also from malonic ester and aqueous KOH, also for such from 25%; perhaps the hydrolysis, which is all the more rapidly effected, the more diluted the potash solution, most rapidly with 1% igem, goes over above potassium compounds. Mono-ethyl malonic acid diethyl ester; for the preparation, one adds to 300 g dry ether and 14.4 g Na (without crushing) 100 g of malonic ester, agitates well, heated to the disappearance of the sodium on the water bath, adds 100 g ethyl iodide, heated, after the reaction diminished up to the neutrality of the mixture on the water bath, initially removed with water, then with diluted Na_2CO_3 -solution and fractional; to the purification one vibrates 75 g briefly with 40 g 25% igem potash, boils insoluble. Oil (67 g) with 25 g KOH in 100 ccm water, registers then unresolved in 25g KOH in 30 g H_2O , removes the diethyl ester by ether

removal, boils with further, 20%igem alkali (so that the quantity of the alkali amounts to 70 g) to about 2 hours, diluted to 1 l, neutralized with HCl and settles with CaCl₂; the salt dried in the vacuum supplies nearly pure ester with the esterification of 46 g; ethyl iodide and 3.6 g powdered potash develop also from 10 g of malonic ester, for 10 g; Kp748, 211° (corrected) under small decomposition; Kp10, 92°; D200, 1.004. Mono methyl malonic acid diethyl ester; from sodium malonic ester in ether was produced, and methyl iodide; one adds KOH powdered by 20 g of malonic ester and 18 g methyl iodide gradually 8 g to a mixture, heated to the accomplished conversion on the water bath, intersperses water too, vibrated well and dries the oil over CaCl₂, - Kp765, 198.5 to 199° (corrected), by alkali one decomposes. Monopropylmalonic acid diethyl ester, Kp771, 225.5 to 226° (corrected), D250, 0.9897. Are event from the Monoalkylmalonic ester prepared to dialkyl malonic ester like these from malonic ester and the effect of Alkyl halide and potash was repeated. Dimethylmalonic acid diethyl ester, Kp765, 196 to 196.5°, becomes slow by KOH of 25%, of 50% rapidly saponified. Diethyl malonic acid diethyl ester, with boiling point of 228.5-229.5° (corrected). For the proof in presence of mono ethyl and malonic ester with 50%igem, then with 25%igem KOH one vibrates briefly; with the diluting with water it separates then in the form of oil droplets: the presence of mono ethyl malonic ester in the diethyl malonic ester indicated by a white precipitate also with 20° saturated KOH solution. Dipropylmalonic acid diethyl ester, with boiling point of 248 to 249°. Ethylacetoacetic acid ethyl ester, from acetoacetic esters C₂H₅I and powdered KOH. Diethylacetoacetic acid ethyl ester, from ethylacetoacetic acid ethyl ester, ethyl iodide and powdered KOH.

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FILE 'CAPLUS' ENTERED AT 09:59:39 ON 18 SEP 2008

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L1      2441 S (?ESTERIFICATION) (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACE
L2      177 S L1 (L) (FAT# OR OIL#)
L3      27 S L2 AND (LIPASE OR ENZYME)
L4      14 S L3 AND FUEL
L5      3 S L1 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)
L6      116 S ALCOHOLYSIS (L) ((METHYL (A) ACETATE) OR (ETHYL (A) ACETATE)
L7      14 S L6 (L) (FAT# OR OIL#)
L8      0 S L7 (L) (FATTY (A) ACID (A) ALKYL (A) ESTER)
L9      0 S L7 AND FUEL
L10     0 S L7 AND (FATTY (A) ACID (A) METHYL (A) ESTER)

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ALL L# QUERIES AND ANSWER SETS ARE DELETED AT LOGOFF

LOGOFF? (Y)/N/HOLD:y

STN INTERNATIONAL LOGOFF AT 10:14:57 ON 18 SEP 2008